

JOURNAL OF THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS

ON ORGANIC CHEMISTRY.

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BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Bromine Derivatives of Tetramethylmethane. PETRU PONI (*Ann. sci. Univ. Jassy*, 1905, 3, 212—216).—Below 0° , the interaction in diffuse daylight between water, bromine, and $\beta\beta$ -dimethylpropane containing some β -methylpropane requires from four to fourteen days according to the intensity of the light. In addition to β -bromo- β -methylpropane, the following substances were isolated by fractional distillation under reduced pressure. *α -Bromo- $\beta\beta$ -dimethylpropane*, $\text{CMe}_3\cdot\text{CH}_2\text{Br}$, is a colourless liquid with an ethereal odour, which boils at $89\text{--}91^{\circ}$ under 749 mm. pressure. It has the sp. gr. 1.294 at $0^{\circ}/0^{\circ}$ and n_D 1.43689 at 20.4° .

β -Bromo- β -methylbutane has been obtained previously by Tissier.

$\alpha\alpha$ -Dibromo- $\beta\beta$ -dimethylpropane, $\text{CMe}_3\cdot\text{CHBr}_2$, is a colourless liquid with a strong ethereal odour, which boils at $64\text{--}65^{\circ}$ under 43 mm. and decomposes when heated under the ordinary pressure. It has the sp. gr. 1.7883 at $0^{\circ}/0^{\circ}$ and n_D 1.50848.

$\alpha\gamma$ -Dibromo- $\beta\beta$ -dimethylpropane, $\text{CH}_2\text{Br}\cdot\text{CMe}_2\cdot\text{CH}_2\text{Br}$, boils at $82\text{--}83^{\circ}$ under 49 mm. and decomposes when heated under the ordinary pressure, has the sp. gr. 1.7052 at $0^{\circ}/0^{\circ}$, and n_D 1.50903 at 20.3° .

The constitution of the last two isomeric compounds is deduced from the law that the boiling point of a disubstituted derivative is the lower the nearer the substituents are together (Henry). C. S.

Preparation of Racemic Amyl Alcohol. PAUL FREUNDLER and E. DAMOND (*Compt. rend.*, 1905, 141, 830—831).—Racemic amyl alcohol, obtained in small quantities by Herzig by reducing tiglic aldehyde (Abstr., 1882, 594) and by Frankland by racemisation of the active alcohol (compare Trans., 1897, 71, 255), can be readily prepared by the condensation of trioxymethylene and magnesium *sec.*-butyl bromide (compare Locquin, Abstr., 1904, i, 546), the yield being 60 per cent. of the theoretical when the calculated quantity of trioxymethylene is added to the magnesium *sec.*-butyl bromide suspended in ether to which a few drops of carbon disulphide have been added to moderate the action, and thus avoid the formation of butylene and butane (compare Bischoff, Abstr., 1905, i, 589; Ahrens and Stapler, *ibid.*, 868). *sec.*-Butyl bromide is obtained by the action of phosphorus tribromide on *sec.*-butyl alcohol, prepared by the direct hydrogenation of methyl ethyl ketone at 140° by the method of Sabatier and Senderens (compare Abstr., 1903, i, 733). M. A. W.

Solubility of Various Salts in Ethylene Glycol. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1905, 275—276, 359).—The solubilities of a number of inorganic salts in ethylene glycol, having the composition $C_2H_6O_2 \cdot H_2O$, at temperatures about 15°, are tabulated. F. G. C. S.

Action of Light on a Solution of Uranyl Sulphate in Ethylene Glycol. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1905, 360).—Uranyl sulphate is dissolved in a small quantity of water, excess of ethylene glycol added, and the whole placed in a flask exposed to sunlight. In two hours, the liquid is quite green, and in $2\frac{1}{2}$ hours uranous sulphate is precipitated. In glycerol, no such action takes place, and even after fifteen months' exposure only a slight green coloration is obtained. This reaction serves to distinguish between ethylene glycol and glycerol. F. G. C. S.

Cetylphosphoric Acid. JOACHIM BIEHRINGER (*Ber.*, 1905, 38, 3974—3977. Compare Tütscheff, *Jahresb.*, 1860, 405).—*Cetyl dihydrogen phosphate (cetylphosphoric acid)*, $C_{16}H_{33}O \cdot PO(OH)_2$, is readily obtained by the action of phosphoric oxide on a solution of cetyl alcohol in dry ether. The ester is not produced in the absence of ether at the same temperature. It forms a snow-white, crystalline powder, is extremely hygroscopic, softens at 60°, and melts at 74°. It dissolves readily in most organic solvents, and reacts as a dibasic acid when titrated with alcoholic potash, using phenolphthalein as indicator.

Sodium, lithium, ferric, lead, and silver salts have been prepared. The salts of the alkaline earths are sparingly soluble. J. J. S.

Action of Ammonia and Amines on Allyl Formate. PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 138—141. Compare Abstr., 1882, 378).—Allyl formate may be prepared conveniently by heating a mixture of glycerol with an equal weight of concentrated formic acid at 125° and finally at 240°; at the

higher temperature, a mixture of allyl formate, allyl alcohol, and a small amount of formic acid distils over, and this is subjected to fractional distillation.

Allyl formate reacts with anhydrous ammonia, slowly if pure, more quickly in presence of a small quantity of allyl alcohol, with development of heat and formation of formamide which melts at 2.4° .

Primary and secondary fatty amines, benzylamine, phenylhydrazine, and piperidine react with allyl formate to form substituted formamides, the rise in temperature being greatest with the primary amines, whilst the reaction with phenylhydrazine takes place without change of temperature.

Formisobutylamide boils at 229° . *Formobenzylamide* melts at 62° and not at 49° , as stated by Holleman (Abstr., 1895, i, 457). *Formodisobutylamide* boils at $227\text{--}228^{\circ}$ (corr.). G. Y.

Action of Ammonia and Amines on Formic Esters of Glycols and Glycerol. II. PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 339—341).—When ammonia gas is absorbed by ethylene diformate, a considerable development of heat occurs, and the product on distillation yields ethylene glycol and somewhat impure formamide. Substituted ammonias (dipropylamine, benzylamine) give pure substituted formamides in very good yield. Similar reactions take place between propylene $\alpha\beta$ -diformate, or the formins of glycerol, and ammonia, dimethylamine, dipropylamine, diisobutylamine, benzylamine, or piperidine, the distillation being performed in a vacuum.

[With W. VAN DORSEN.]—The reaction is applicable to the formic esters of unsaturated glycols, formobenzylamide having been obtained by distilling a mixture of benzylamine and $\gamma\delta$ -dihydroxy- $\Delta^{\alpha\epsilon}$ -hexadiene diformate. C. S.

Acetic Arsenious Anhydride. AMÉ PICTET and A. BON (*Bull. Soc. chim.*, 1905, [iii], 33, 1139—1143. Compare Abstr., 1903, i, 309, 601).—*Triacetic arsenious anhydride*, $\text{As}(\text{OAc})_3$, prepared by dissolving arsenious oxide in acetic anhydride, crystallises in colourless needles, melts at 82° , distils at $165\text{--}170^{\circ}$ under 31 mm. pressure, is readily soluble in chloroform or ethyl acetate, less so in cold benzene, and almost insoluble in light petroleum or carbon disulphide. It decomposes in moist air forming the two corresponding acids, and is attacked by alcohols yielding the corresponding alkyl arsenite and acetate. Glyceryl and phenyl arsenites were prepared in this way.

When fused with benzoic acid, triacetic arsenious anhydride furnishes acetic acid and *tribenzoic arsenious anhydride*, $\text{As}(\text{OBz})_3$. This occurs as a white, crystalline mass, melts at 155° , and decomposes rapidly on exposure to air, forming benzoic and arsenious acids. It dissolves readily in chloroform, less so in benzene or ethyl acetate, and very little in light petroleum or carbon disulphide. T. A. H.

Preparation of Anhydrides of Monobasic Acids. VEREIN FÜR CHEMISCHE INDUSTRIE (D.R.-P. 161882).—Acid anhydrides are readily prepared by the action of sulphuryl chloride on the alkali salts

of the corresponding acids, but large quantities of acid chloride are obtained when alkaline earth salts are substituted. It is found, however, that a mixture of the two salts gives satisfactory results, even 10—15 per cent. of sodium acetate mixed with calcium acetate being sufficient to prevent the formation of acetyl chloride.

C. H. D.

Crotonic and isoCrotonic Acids. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1905, 274—275. Compare Abstr., 1905, i, 321, 628).—Crotonic acid dissolves in warm sulphuric acid and becomes charred, *isocrotonic* acid forms a light brown solution becoming dark brown, garnet-red, and black, depositing a flocculent precipitate of carbon.

On heating gradually with a large excess of sulphuric acid, both acids char and evolve carbon dioxide and then sulphur dioxide.

F. G. C. S.

Preparation of Oxalates from Formates. RUDOLF KOEFF & Co. (D.R.-P. 161512).—The conversion of formates into oxalates by heat takes place quantitatively when about 1 per cent. of alkali hydroxide is added to the mass before heating. The alkali appears to exert a catalytic influence. In the case of sodium formate containing 1 per cent. of sodium hydroxide, evolution of hydrogen begins at 290°, and at 360° the mass is completely converted into white, porous oxalate. Alkali peroxides, plumbates, amides, ethoxides, or phenoxides may also be used.

C. H. D.

Ester Anhydrides of Dibasic Acids. D. MOL (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 336—337).—*Ethyl anhydro-oxalate*, $O(CO \cdot CO_2Et)_2$, obtained by the action of ethyloxalyl chloride on potassium ethyl oxalate covered with ether, distils at 85—90° under less than 1 mm. pressure; the distillate solidifies on cooling and melts at 4°. The anhydride, which is also obtained by acting on an excess of potassium ethyl oxalate with phosphorus oxychloride, decomposes when heated at the ordinary pressure.

C. S.

Derivatives of Trimethylparaconic and Camphoronic Acids. WILLIAM A. NOYES and HOWARD W. DOUGHTY (*J. Amer. Chem. Soc.*, 1905, 27, 1429—1435).—Noyes and Patterson (Abstr., 1902, i, 742) have shown that when ethyl trimethylitamate is treated with phosphorus tribromide, it is converted into ethyl trimethylparaconate. As the ester used in this experiment was not pure, it was considered desirable to ascertain the action of phosphorus tribromide on methyl trimethylitamate. *Methyl trimethylitamate* was obtained as a yellow oil which boils at 122—127° under 12—14 mm., and at 261—265° under atmospheric pressure. When this ester was treated with hydrobromic acid or phosphorus tribromide, methyl trimethylparaconate could not be obtained. Attempts to prepare an acetyl or a benzoyl derivative of the ester were unsuccessful. It was found impossible to reduce trimethylparaconic acid electrolytically, the acid being recovered from the experiments unchanged.

When ethyl trimethylsuccinate is heated with ethyl chloroacetate in presence of sodium or sodium ethoxide, no trace of camphoronic acid is produced. Attempts were made to effect the condensation of chloral with sodium trimethylsuccinate, but without success.

i-Bromoanhydrocamphoronic chloride, obtained by the method used by Aschan (Abstr., 1895, i, 188) in the preparation of the active form, crystallises from ether, and melts at 123—126°. *i-Camphoronic anhydride* distils at 193—194° under 20 mm. pressure, solidifies as a white, crystalline mass, melts at 119—121°, and is readily soluble in water and sparingly so in ether. *i-Camphoronic acid* crystallises in pyramids, and, on heating, partly sublimes and melts at 190—191°.

E. G.

Trithioformaldehyde and a New Method of preparing Trimethylsulphonium Iodide. ALBERT REYCHLER (*Bull. Soc. chim.*, 1905, [iii], 33, 1226—1232. Compare Klinger, Abstr., 1879, 132).—Trithioformaldehyde may be purified by recrystallisation from hot aniline and subsequently washing with hydrochloric acid and alcohol. It reacts with methyl iodide when a mixture of the two substances is heated in closed vessels at 80° to 100°, forming trimethylsulphonium iodide; the yield of the latter under these conditions is small, and the reaction goes better in presence of methyl alcohol, when a yield of trimethylsulphonium iodide equivalent to from 85 to 90 per cent. of the theoretical is obtainable. The reaction may be represented by the following equations: $(\text{CH}_2\text{S})_3 + 3\text{MeI} + 6\text{MeOH} = 3\text{SMe}_3\text{I} + 3\text{CH}_2(\text{OH})_2$ and $3\text{CH}_2(\text{OH})_2 + 6\text{MeOH} = 6\text{H}_2\text{O} + 3\text{CH}_2(\text{OMe})_2$. The presence of methylal in the by-products of the reaction was proved.

The reaction becomes much more complex when ethyl iodide is substituted for methyl iodide or ethyl alcohol for methyl alcohol.

The author notes that this breaking down of the molecule of trithioformaldehyde by such a reagent as methyl iodide is remarkable in view of the stability of the polymeride towards other reagents.

T. A. H.

Crystals of *s*-Tetrachloroisopropylformal. F. KAISIN (*Bull. Acad. roy. Belg.*, 1905, 276—277).—A correction to a former paper (Abstr., 1905, i, 261). The crystallographic data for *s*-tetrachloroisopropylformal should be $[a : b : c = 2.789 : 1 : 1.384]$.

F. G. C. S.

Action of Hydrogen Cyanide on Ketones. A. J. ULTEE (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 141—144).—Acetone and hydrogen cyanide react in aqueous solution in presence of a small quantity of a base with development of heat to form the cyanohydrin (hydroxyisobutyronitrile), which, as the reaction is reversible, can be isolated by distillation only after neutralisation of the base. That the same equilibrium is reached by adding a trace of potassium hydroxide to a molecular mixture of acetone and hydrogen cyanide or to the cyanohydrin in aqueous solution is proved by the refractions n_D 1.39721 and 1.39818 at 12° for the two solutions respectively. Determinations of the free hydrogen cyanide present show that the amount of the cyanohydrin formed at 0° is 94.5, and at 25° is 88.60 per cent. of the

theoretical. The corresponding values for methyl ethyl ketone are 95.57 and 90.36, for diethyl ketone 95.90 and 91.29 per cent. respectively.

On mixing anhydrous hydrogen cyanide with anhydrous acetone, there is a slight rise in temperature, but no interaction takes place even after six months, as shown by determinations of the free hydrogen cyanide present and by the unchanged refraction of the mixture. Pure cyanohydrins may be obtained by adding a slight excess of fuming hydrochloric acid to potassium cyanide covered by a ketone and distilling the product under reduced pressure.

Hydroxyisobutyronitrile melts at -19.5° to a colourless liquid which boils at 82° under 23 mm., decomposes on distillation under the atmospheric pressure, and has the sp. gr. 0.9342 at 18° and n_D 1.40526 at 8.5° .

α -Hydroxy- α -methylbutyronitrile, from methyl ethyl ketone, is a colourless liquid having a faint ketonic odour, boils at 91° under 20.5 mm., does not solidify in a paste of solid carbon dioxide and acetone, and has the sp. gr. 0.9324 at 18.5° and n_D 1.41775 at 12.5° .

α -Hydroxy- α -ethylbutyronitrile, prepared from diethyl ketone, is a colourless liquid which boils at 97.5° under 18.5 mm. pressure, does not solidify when cooled with solid carbon dioxide and acetone, and has the sp. gr. 0.9300 at 18.5° and n_D 1.42585 at 18° . G. Y.

Triacetylcellulose. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 159524. Compare Skraup, Abstr., 1899, i, 852; Franchimont, Abstr., 1900, i, 141).—Acetic anhydride and sulphuric acid act on cellulose below 50° , preferably in presence of glacial acetic acid, to form *triacetylcellulose*. The product dissolves readily in chloroform, epichlorohydrin, nitrobenzene, or acetic acid, but is insoluble in alcohol, ether, glycerol, or amyl acetate. It decomposes at about 250° , and is very resistant towards alkali hydroxides or dilute acids. On evaporation of its solutions, it forms colourless films which are perfectly flexible even at a thickness of 0.5 mm., and do not become brittle with time. Very voluminous gelatinous masses are obtained when the concentrated solutions are poured into water or alcohol. C. H. D.

Action of Bromine on Trimethylamine. JAMES F. NORRIS (*Ber.*, 1905, 38, 3904—3906).—Hantzsch and Graf's product, obtained by the action of bromine on trimethylamine (Abstr., 1905, i, 575), is not identical with Remsen and Norris' trimethylamine dibromide (Abstr., 1896, i, 336), which melts at 117 — 119° and for which the formula $NMe_3 \cdot HBr \cdot Br$ is now confirmed (Abstr., 1898, i, 169). The author considers that Hantzsch and Graf's substance may be the primary reaction-product, which changes easily into Remsen and Norris' dibromide. G. Y.

Conversion of Formhydroxamic Acid into Fulminic Acid. HENRY C. BIDDLE (*Ber.*, 1905, 38, 3858—3859. Compare Abstr., 1900, i, 137).—A reply to Wöhler (Abstr., 1905, i, 419). In order to secure the conversion of chloro-formoxime acetate by the action of silver nitrate into silver fulminate, it is necessary to allow the

mixed solutions to remain for twenty-four hours; the silver fulminate is somewhat soluble in water and might be overlooked when the precipitate is digested with much boiling water. T. M. L.

Compounds of Metallic Thiocyanates with Organic Bases. HERMANN GROSSMANN and FRITZ HÜNSELER (*Zeit. anorg. Chem.*, 1905, **46**, 361—405. Compare *Abstr.*, 1904, i, 341).—The additive compounds, such as $\text{Ni}(\text{SCN})_2 \cdot 2\text{C}_5\text{H}_5\text{NH}_2$, were usually prepared by the action of an aqueous or alcoholic solution of the metallic thiocyanate on an alcoholic solution of the base, crystals in some cases separating at once.

The double salts, such as $\text{Ni}(\text{NH}_3\text{Ph})_2(\text{SCN})_3$, were usually prepared by dissolving the corresponding additive compounds in thiocyanic acid and evaporating the solution if necessary.

Pyridine mercuric thiocyanate, $\text{Hg}(\text{SCN})_2 \cdot \text{C}_5\text{H}_5\text{N}$, forms colourless, transparent, monoclinic crystals. *Pyridiniummercuric thiocyanate*, $\text{HgC}_5\text{H}_5\text{N}(\text{SCN})_3$, is a colourless, crystalline mass. *Pyridiniummercuric chloride*, $\text{Hg}(\text{C}_5\text{H}_5\text{N})_3\text{Cl}_3$, and *bromide* form long, prismatic, triclinic crystals; the *iodide* long, slender, yellow, lustrous needles. *Pyridiniummercuric chlorobromide*, $\text{HgBr}_2 \cdot \text{C}_5\text{H}_5\text{NCl}$, occurs in long, prismatic, colourless, monoclinic crystals; the *chloroiodide*,

$\text{HgI}_2 \cdot 2\text{C}_5\text{H}_5\text{NBr}$, forms yellow, not well-defined crystals. $2\text{HgI}_2 \cdot 3\text{C}_5\text{H}_5\text{NCl}$ occurs in four-sided, monoclinic prisms; the *chlorocyanide*, $3\text{Hg}(\text{CN})_2 \cdot 2\text{C}_5\text{H}_5\text{NCl}$, forms long, prismatic, monoclinic crystals.

Cobalt thiocyanate, $\text{Co}(\text{SCN})_2 \cdot 4\text{H}_2\text{O}$, forms glistening, wine-red, rhombic crystals which gradually become brown and opaque in the air (compare Rosenheim and Cohn, *Abstr.*, 1901, i, 456).

Tetrapyridine cobalt thiocyanate, $\text{Co}(\text{SCN})_2 \cdot 4\text{C}_5\text{H}_5\text{N}$, crystallises in rose-coloured needles.

Tripyridiniumcobalt thiocyanate, $\text{Co}(\text{C}_5\text{H}_5\text{N})_3(\text{SCN})_5$, forms dark blue, monoclinic crystals, which show mixed colours. A *dipyridinium* compound can also be obtained. All complex cobalt thiocyanates are blue in alcoholic and concentrated aqueous solution, but are split up into their components by excess of water, the solution becoming rose-coloured.

Dipyridiniumnickel thiocyanate, $\text{Ni}(\text{C}_5\text{H}_5\text{N})_2(\text{SCN})_4$, forms green, hemispherical crystals.

Tetrapyridine ferrous thiocyanate, $\text{Fe}(\text{SCN})_2 \cdot 4\text{C}_5\text{H}_5\text{N}$, forms yellow, lustrous, prismatic crystals, which do not readily oxidise in the air. *Tripyridiniumferrous thiocyanate*, $\text{Fe}(\text{C}_5\text{H}_5\text{N})_3(\text{SCN})_5$, and the corresponding *manganous* compound, $\text{Mn}(\text{C}_5\text{H}_5\text{N})_3(\text{SCN})_5$, are obtained respectively in yellow crystals which slowly become red in the air and in well-defined, colourless crystals. The cobalt, ferrous, and manganous compounds are isomorphous.

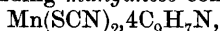
Dipyridiniumzinc iodide, $\text{Zn}(\text{C}_5\text{H}_5\text{N})_2\text{I}_4$, forms yellow, monoclinic crystals. *Pyridinium thiocyanate*, $\text{C}_5\text{H}_5\text{N} \cdot \text{SCN}$, obtained by evaporating molecular amounts of its components, separates in transparent, odourless, hygroscopic crystals.

Quinoline cadmium thiocyanates, $\text{Cd}(\text{SCN})_2 \cdot 2\text{C}_9\text{H}_7\text{N}$ and $\text{Cd}(\text{SCN})_2 \cdot 3\text{C}_9\text{H}_7\text{N}$,

are obtained as yellowish-white, microscopic, prismatic crystals. *Di- and tetra-quinoliniumcadmium thiocyanates*, $\text{Cd}(\text{C}_9\text{H}_8\text{N})_2(\text{SCN})_4$ and $\text{Cd}(\text{C}_9\text{H}_8\text{N})_4(\text{SCN})_6$, form transparent, monoclinic crystals, which rapidly become opaque in the air. *Diquinoliniumcadmium bromide*, $\text{Cd}(\text{C}_9\text{H}_8\text{N})_2\text{Br}_4 \cdot \text{H}_2\text{O}$, occurs in transparent, colourless, monoclinic crystals; the corresponding *iodide* in yellow crystals. *Quinoline mercuric thiocyanate*, $\text{Hg}(\text{SCN})_2 \cdot \text{C}_9\text{H}_7\text{N}$, forms colourless crystals; the salts $\text{Hg}(\text{C}_9\text{H}_8\text{N})_2(\text{SCN})_4$; $\text{Hg}(\text{C}_9\text{H}_8\text{N})_4(\text{SCN})_6$; $\text{HgBr}_2 \cdot 2\text{C}_9\text{H}_8\text{NBr}$, and $\text{HgI}_2 \cdot 2\text{C}_9\text{H}_8\text{NI}$ were also prepared; the two former crystallise in glancing, prismatic needles, the *iodide* in yellow, microscopic needles.

Of the *quinoline cobalt* compounds: $\text{Co}(\text{SCN})_2 \cdot 2\text{C}_9\text{H}_7\text{N} \cdot 2\text{H}_2\text{O}$, occurring in well-formed, dark blue, glancing crystals; $\text{Co}(\text{C}_9\text{H}_8\text{N})_3(\text{SCN})_4$; $\text{Co}(\text{C}_9\text{H}_8\text{N})_2\text{Cl}_4 \cdot 2\text{H}_2\text{O}$; $\text{CoBr}_2 \cdot 2\text{C}_9\text{H}_7\text{N}$, and $\text{Co}(\text{C}_9\text{H}_8\text{N})_2\text{Br}_4 \cdot 2\text{H}_2\text{O}$ were prepared by the general methods. The chloride occurs in grass-green, tabular crystals, the other three in lustrous, dark blue crystals. The *nickel* compounds, $\text{Ni}(\text{SCN})_2 \cdot 4\text{C}_9\text{H}_7\text{N}$ and $\text{Ni}(\text{C}_9\text{H}_8\text{N})_4(\text{SCN})_6$, occur in green crystals.

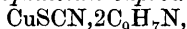
Tetraquinoline ferrous thiocyanate, $\text{Fe}(\text{SCN})_2 \cdot 4\text{C}_9\text{H}_7\text{N}$, forms colourless, prismatic needles, which become red in the air; *tetraquinolinium-ferrous thiocyanate*, $\text{Fe}(\text{C}_9\text{H}_8\text{N})_4(\text{SCN})_6$, occurs in prismatic, glancing, wine-red crystals, which become dark brown in the air owing to oxidation. The corresponding *manganese* compounds,



yellowish-white, well-formed plates, and $\text{Mn}(\text{C}_9\text{H}_7\text{N})_4(\text{SCN})_6$, flesh-coloured, lance-shaped crystals, were prepared. No other quinoline thiocyanate compounds of these three metals could be obtained. The tetraquinolinium compounds of mercury, cadmium, cobalt, nickel, iron, and manganese are isomorphous.

Zinc compounds: $\text{Zn}(\text{SCN})_2 \cdot 2\text{C}_9\text{H}_7\text{N}$ crystallises in microscopic needles; $\text{Zn}(\text{C}_9\text{H}_8\text{N})_2(\text{SCN})_4$ forms milky, prismatic needles. $\text{Zn}(\text{C}_9\text{H}_8\text{N})_2\text{Cl}_2$ and the corresponding *bromide* and *iodide* occur in transparent, monoclinic crystals and are isomorphous.

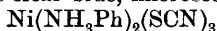
Diquinoline silver thiocyanate, $\text{AgSCN} \cdot 2\text{C}_9\text{H}_7\text{N}$, forms glistening, milky, regular prisms, which are decomposed by water. No double salt could be obtained. *Diquinoline cuprous thiocyanate*,



crystallises from alcohol in glancing, yellowish-red prisms. The corresponding *chloride* and *bromide* were obtained.

Quinoline thiocyanate, $\text{C}_9\text{H}_8\text{N} \cdot \text{SCN}$, is prepared like the corresponding pyridine compounds, from which it differs in being more stable and in showing greater tendency to crystallise. It occurs in well-formed, clear, monoclinic crystals.

The *aniline* compounds so far obtained contain two molecules of the base, and are characterised by their great stability. $\text{Cd}(\text{SCN})_2 \cdot 2\text{NH}_2\text{Ph}$ crystallises in prismatic needles. $\text{Cd}(\text{NH}_2\text{Ph})_2(\text{SCN})_4$ forms colourless, glistening, columnar crystals. $\text{Hg}(\text{SCN})_2 \cdot 2\text{NH}_2\text{Ph}$ forms colourless, columnar crystals; $\text{Hg}(\text{NH}_2\text{Ph})_2(\text{SCN})_4$, colourless, lustrous needles. $\text{Co}(\text{SCN})_2 \cdot 2\text{NH}_2\text{Ph}$ crystallises in prismatic, greyish-violet needles. $\text{Co}(\text{NH}_2\text{Ph})_2(\text{SCN})_3$ forms lustrous, dark blue, microscopic crystals. $\text{Ni}(\text{SCN})_2 \cdot 2\text{NH}_2\text{Ph}$ forms clear blue, microscopic needles.



is a clear green, crystalline powder. $\text{Fe}(\text{SCN})_3 \cdot 2\text{NH}_2\text{Ph}$ forms glistening, yellowish-white needles. $\text{Fe}(\text{NH}_3\text{Ph})(\text{SCN})_3$ forms red crystals and is comparatively unstable. $\text{Mn}(\text{SCN})_2 \cdot 2\text{NH}_2\text{Ph}$ crystallises in regular, six-sided, columnar crystals. $\text{Mn}(\text{NH}_3\text{Ph})_2(\text{SCN})_3$ forms a yellow, crystalline powder. $\text{Zn}(\text{SCN})_2 \cdot 2\text{NH}_2\text{Ph}$ is obtained in well-formed, glistening, columnar crystals. $\text{Zn}(\text{NH}_3\text{Ph})_2(\text{SCN})_3$ forms long, glistening, colourless prisms; both salts redden in the air.

Phenylhydrazine Compounds.— $\text{Cd}(\text{SCN})_2 \cdot 5\text{N}_2\text{H}_3\text{Ph}$ forms long, glistening needles. $\text{Cd}(\text{SCN})_2 \cdot 2\text{N}_2\text{H}_3\text{Ph}$ resembles the penta-compound. $\text{Cd}(\text{N}_2\text{H}_4\text{Ph})_4(\text{SCN})_6$ forms colourless, lustrous, microscopic needles. Mercury compounds with phenylhydrazine could not be obtained owing to the reducing action of the latter substance. $\text{Ni}(\text{SCN})_2 \cdot 4\text{N}_2\text{H}_3\text{Ph}$ and $\text{Ni}(\text{SCN})_2 \cdot 6\text{N}_2\text{H}_3\text{Ph}$ both form blue, microscopic crystals, which become dirty-brown on exposure to air. $\text{NiBr}_2 \cdot 6\text{N}_2\text{H}_3\text{Ph}$ resembles the corresponding thiocyanate. $\text{Co}(\text{SCN})_2 \cdot 6\text{N}_2\text{H}_3\text{Ph}$ and $\text{Co}(\text{SCN})_2 \cdot 4\text{N}_2\text{H}_3\text{Ph}$ crystallise in rose-red, microscopic needles which turn brown in the air. $\text{Co}(\text{N}_2\text{H}_4\text{Ph})_4(\text{SCN})_6$ forms green, shining, microscopic needles. $\text{Fe}(\text{SCN})_2 \cdot 6\text{N}_2\text{H}_3\text{Ph}$ crystallises in yellowish-white, well-formed, microscopic needles; the corresponding *bromide* and *iodide* form yellowish-white, microscopic crystals. $\text{Mn}(\text{SCN})_2 \cdot 6\text{N}_2\text{H}_3\text{Ph}$ crystallises in long needles with a silvery lustre and turns brown in the air. $\text{Mn}(\text{N}_2\text{H}_4\text{Ph})_3(\text{SCN})_5$ forms colourless, glistening, microscopic needles. $\text{Zn}(\text{SCN})_2 \cdot 6\text{N}_2\text{H}_3\text{Ph}$ and $\text{Zn}(\text{SCN})_2 \cdot 2\text{N}_2\text{H}_3\text{Ph}$ crystallise in long, prismatic needles. $\text{ZnBr}_2 \cdot 5\text{N}_2\text{H}_3\text{Ph}$ forms slender, colourless crystals.

It is pointed out that there is great analogy between the halogen compounds and those containing the thiocyanate group both as regards the type of compounds formed and the crystallographic relationships.

G. S.

Presence of ψ -Cumene in Roumanian Petroleum. PETRU PONI (*Ann. sci. Univ. Jassy*, 1905, 3, 217—218).—By the nitration of the fractions boiling between 160 — 161° and 170 — 172° , ψ -cumene was detected in the form of its trinitro-derivative, which crystallises in short, quadratic prisms melting at 184 — 185° .

C. S.

Chlorination by means of Sulphuryl Chloride. ALFRED WOHL (D.R.-P. 160102 and 162394. Compare *Abstr.*, 1904, i, 283).—In chlorination by means of sulphuryl chloride, the hydrogen chloride and sulphur dioxide evolved carry with them much sulphuryl chloride, which cannot be recovered completely by cooling. It is, therefore, advisable to pass the vapours through fuming sulphuric acid. The chlorosulphonic acid thus obtained is readily reconverted into sulphuryl chloride. It is still more advantageous to use as absorbing liquid the same compound, such as toluene, as that undergoing chlorination in the principal apparatus, a little acetyl chloride being added to facilitate the reaction.

C. H. D.

The Six Isomeric Tribromoxylenes. F. M. JAEGER and JAN J. BLANKSMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 153—155. Compare Jaeger, *Abstr.*, 1903, i, 240).—The six possible

tribromoxylenes have been prepared by the following series of reactions :

On bromination in glacial acetic acid solution, 1 : 2 : 3-xylylidine yields 4 : 6-dibromo-1 : 2 : 3-xylylidine, which melts at 56°, and by means of Sandmeyer's reaction is converted into 3 : 4 : 6-tribromo-o-xylene, melting at 86.5°.

In the same manner, 1 : 2 : 4-xylylidine yields 3 : 5-dibromo-1 : 2 : 4-xylylidine, which melts at 63° and is converted into 3 : 4 : 5-tribromo-o-xylene, melting at 105°.

2 : 4 : 6-Tribromo-m-xylene, which melts at 85°, is obtained in three ways : (1) by elimination by means of amyl nitrite and copper powder of the amino-group of 2 : 4 : 6-tribromo-1 : 3 : 5-xylylidine, which is obtained by bromination of *s*-xylylidine, and melts at 195°. (2) From 4 : 6-dibromo-1 : 3 : 2-xylylidine by Sandmeyer's reaction. (3) By Sandmeyer's reaction from 2 : 6-dibromo-1 : 3 : 4-xylylidine, which is formed by hydrolysis of 2 : 6-dibromoaceto-1 : 3 : 4-xylylidine and melts at 65°.

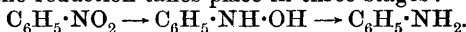
4 : 5 : 6-Tribromo-m-xylene, which melts at 105°, was obtained in two ways : (1) by elimination of the amino-group of 4 : 5 : 6-tribromo-1 : 3 : 2-xylylidine, which is formed by bromination of 4 : 6-dibromo-1 : 3 : 2-xylylidine and melts at 190°. (2) By Sandmeyer's reaction from 5 : 6-dibromo-1 : 3 : 4-xylylidine, which is formed by bromination of 6-bromo-1 : 3 : 4-xylylidine and melts at 35°.

2 : 4 : 5-Tribromo-m-xylene, which melts at 87°, was formed by Sandmeyer's reaction from 4 : 5-dibromo-1 : 3 : 2-xylylidine, which is obtained by brominating 4-bromo-1 : 3 : 2-xylylidine and melts at 50°.

2 : 3 : 5-Tribromo-p-xylene is formed from 3 : 5-dibromo-1 : 4 : 2-xylylidine and melts at 89°.

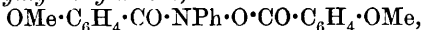
G. Y.

Chemical Action of Light. X. GIACOMO CIAMICIAN and PAUL SILBER (*Ber.*, 1905, 38, 3813—3824. Compare *Abstr.*, 1901, i, 36, 329, 390, 547 ; 1902, i, 433 ; 1903, i, 39, 171, 562, 626 ; 1904, i, 161 ; 1905, i, 335, 414).—Under the influence of light, alcoholic solutions of nitrobenzene yield not only aniline, but a small fraction of a substance soluble in alkali, which is shown to be *p*-aminophenol, proving that the reduction takes place in three stages :



The basic fraction contains, in addition to aniline, quinaldine, 2-methyl-3-ethylquinoline, or 2-isopropyl-3-isobutylquinoline, according as ethyl, propyl, or isoamyl alcohol is used as solvent. The ethyl-alcoholic solution gives also a *base*, $\text{C}_6\text{H}_7\text{O}_2\text{N}$, which crystallises from light petroleum in stout, colourless scales, melts at 70—71°, and reduces Fehling's solution and gold chloride ; its *acetyl* derivative, $\text{C}_8\text{H}_9\text{O}_3\text{N}$, separates from hot water in large crystals and melts at 178—179° ; its *picrate*, $\text{C}_{12}\text{H}_{10}\text{O}_9\text{N}_4$, forms yellow needles and melts at 185°, its *benzoyl* derivative, $\text{C}_8\text{H}_6\text{O}_2\text{N}\cdot\text{COPh}$, crystallises from methyl alcohol in rhombic tablets and melts at 192°. The base probably arises from an impurity in the nitrobenzene.

The action of light on a mixture of anisaldehyde and nitrobenzene gives anisic acid, dianisoylphenylhydroxylamine, anisoylanilide, and azoxybenzene and *o*-hydroxyazobenzene (derived from nitrosobenzene).

Dianisoylphenylhydroxylamine,

crystallises from methyl alcohol in colourless prisms melting at 150°.

Experiments were also tried with vanillin, piperonal, salicylaldehyde, and cinnamaldehyde, which yield the corresponding acids, but the ketones, acetone and acetophenone, were found to be without action on the nitrobenzene.

T. M. L.

Nitration of *s*-Nitro-*m*-xylene. JAN J. BLANKSMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 70—74. Compare Abstr., 1902, i, 442, 600).—The action of a mixture of nitric and sulphuric acids on *s*-nitro-*m*-xylene leads to the formation of 4:5:6-trinitro-*m*-xylene, together with a smaller quantity of the 2:4:5-trinitro-compound.

4:5:6-*Trinitro-m-xylene* crystallises from alcohol in long, colourless, monoclinic needles or rods [$a:b:c = 0.5950:1:0.2706$; $\beta = 88^\circ 11'$], melts at 125°, and, when treated with alcoholic methylamine, is converted into 4:6-dinitromethyl-1:3:5-*xylylidine*, $\text{C}_6\text{HMe}_2(\text{NO}_2)_2 \cdot \text{NHMe}$, which melts at 85°, and on bromination yields 2-bromo-4:6-dinitromethyl-1:3:5-*xylylidine*, melting at 146°. On treatment with nitric acid, this forms 4-bromo-2:6-dinitro-3:5-dimethylphenylmethylnitroamine, $\text{C}_6\text{Me}_2(\text{NO}_2)_2 \cdot \text{Br} \cdot \text{NMe} \cdot \text{NO}_2$, which melts at 103°.

2:4:5-*Trinitro-m-xylene* separates from alcohol in triclinic crystals [$a:b:c = 2.8359:1:0.8510$; $\alpha = 100^\circ 54'$, $\beta = 106^\circ 59'$, $\gamma = 117^\circ 51\frac{1}{2}'$], melts at 90°, and on treatment with alcoholic methylamine is converted into 2:4-dinitromethyl-1:3:5-*xylylidine*, which melts at 127°, and on bromination yields 6-bromo-2:4-dinitromethyl-1:3:5-*xylylidine*, melting at 175°. This is formed also by the action of alcoholic methylamine on 6-bromo-2:4:5-trinitro-*m-xylene*, which melts at 183°, and is obtained by nitrating 6-bromo-5-nitro-*m-xylene*, melting at 56°, or on 5:6-dibromo-2:4-dinitro-*m-xylene*, which melts at 193° and is obtained by nitrating 5:6-dibromo-*m-xylene*, melting at 11°. 6-Bromo-2:4-dinitro-3:5-dimethylphenylmethylnitroamine, formed by the action of nitric acid on 6-bromo-2:4-dinitromethyl-1:3:5-*xylylidine*, melts at 152°.

Whilst the action of a mixture of nitric acid of sp. gr. 1.52 and sulphuric acid on 6-bromo- and on 6-chloro-5-nitro-*m-xylene* leads respectively to the formation of 6-bromo- and 6-chloro-2:4:5-trinitro-*m-xylene*, which melts at 165°, 6-iodo-5-nitro- and 6-iodo-4-nitro-*m-xylene* yield, on nitration, 4:5:6-trinitro- and 2:4:6-trinitro-*m-xylenes*, respectively. 6-Iodo-5-nitro-*m-xylene*, formed by Sandmeyer's reaction from 5-nitro-1:3:4-*xylylidine*, melts at 165°.

2:4:6-*Trinitro-m-xylene* separates from a mixture of benzene and alcohol in large, thick, prismatic, bipyramidal, rhombic crystals [$a:b:c = 0.6587:1:0.5045$], melts at 182°, and of the three trinitro-*m-xylenes* is the least soluble in alcohol, the most soluble being the 2:5:6-trinitro-compound melting at 90°.

On treatment with nitric acid of sp. gr. 1.52 at the laboratory temperature, *s*-nitro-*m-xylene* yields 4:5-dinitro-*m-xylene*, which, on nitration with a mixture of nitric and sulphuric acids, forms chiefly 4:5:6-trinitro-*m-xylene*. An attempt to convert this into tetranitro-*m-xylene* by the action of nitric and sulphuric acids at 150°, leads to

the formation of a small quantity of an acid oxidation *product*, forming colourless crystals and melting at 190°. G. Y.

Palladium. ALEXANDER GUTBIER and A. KRELL (*Ber.*, 1905, **38**, 3869—3873. Compare Abstr., 1905, i, 876; ii, 584).—*Palladous methylaniline chloride*, $(\text{NH}_2\text{MePhCl})_2\text{PdCl}_2$, crystallises from dilute alcohol in broad, brown needles. The *bromide*, $(\text{NH}_2\text{MePhBr})_2\text{PdBr}_2$, crystallises in reddish-brown needles from hydrobromic acid and in plates from dilute alcohol.

Palladous ethylaniline chloride, $(\text{NH}_2\text{EtPhCl})_2\text{PdCl}_2$, was obtained in brown needles from hydrochloric acid and in large, brown plates from dilute alcohol. The *bromide*, $(\text{NH}_2\text{EtPhBr})_2\text{PdBr}_2$, separates in well-formed brown needles from hydrobromic acid, and in clusters of pyramidal crystals from dilute alcohol.

Palladous diethylaniline chloride, $(\text{NH}_2\text{Et}_2\text{PhCl})_2\text{PdCl}_2$, crystallises in dark brown spangles from hydrochloric acid and in dark yellowish-brown needles from dilute alcohol. The corresponding *bromide* forms large, reddish-brown needles and plates.

Diphenyldimethylpalladosammine chloride, $\text{Pd}(\text{NHMePh})_2\text{Cl}_2$, forms golden-yellow, microcrystalline needles. The *bromide* forms yellowish-red plates.

Diphenyldiethylpalladosammine chloride, $\text{Pd}(\text{NH}_2\text{EtPh})_2\text{Cl}_2$, is a very sparingly soluble, yellow precipitate. The *bromide* crystallises from much dilute alcohol in dark yellow scales with a green lustre.

T. M. L.

A New Dinitrodiphenylamine. FRIEDRICH KEHRMANN and ROBERT KAISER (*Ber.*, 1905, **38**, 3778—3779).—2:6-Dinitrodiphenylamine, $\text{NHPh}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$, is formed together with 2:4-dinitrodiphenylamine by heating 1-chloro- or 1-iodo-2:4-dinitrobenzene, containing small quantities of the 2:6-dinitro-isomerides, with aniline. It crystallises in red prisms, melts at 106°, is easily soluble in boiling alcohol or glacial acetic acid, and forms an almost colourless solution in concentrated sulphuric acid. G. Y.

Nitrodiphenylamines. PAUL JUILLARD (*Bull. Soc. chim.*, 1905, [iii], **33**, 1172—1190. Compare Abstr., 1905, i, 843).—Most of the substances described in this paper were prepared for purposes of comparison with the nitration products of Orange IV (anilinobenzene-azobenzene-*p*-sulphonic acid, *loc. cit.*). The following new products were obtained.

2:4'-Dinitrodiphenylnitrosoamine is prepared by nitrating, under specified conditions, 2-nitrodiphenylnitrosoamine dissolved in acetic acid; it crystallises in colourless leaflets with a faint pink tint, melts and decomposes at 160—162°, is readily soluble in alcohol, less so in acetone, and slightly so in toluene. Boiling alcohol converts it into 2:4'-dinitrodiphenylamine (m. p. 217—219°). A mixture of this nitrosoamine with its isomeride, 2:2'-dinitrodiphenylnitrosoamine, is produced when the nitration is carried out under certain other conditions; the mixture (molecular combination?) melts and

decomposes into the two corresponding dinitrophenylamines at about 140°.

4:4'-*Dinitrodiphenylnitrosoamine* is produced when nitroso-*p*-nitro-orange IV, freshly prepared, is dissolved in dilute nitric acid (33 per cent.) kept at 0°. It crystallises in large, faintly orange-coloured prisms, melts and decomposes at 150°, and is converted by boiling alcohol into 4:4'-dinitrodiphenylamine. A mixture of this nitrosoamine with its isomeric, 2:4'-dinitrodiphenylnitrosoamine, was obtained by Witt and Nietzke (*Ber.*, 1879, 12, 1400).

2:2'-*Dinitrodiphenylamine* is obtained by heating *o*-nitrodiphenylnitrosoamine, dissolved in acetic acid; it crystallises in golden-yellow laminae, melts at 166–167°, and is readily soluble in most organic solvents. Nitric acid converts it into 2:4:2'-trinitrodiphenylamine (m. p. 183–184°), a reaction which may be used for its characterisation.

2:4:2'-*Trinitrodiphenylamine* may be prepared by heating 2:4-dinitrobromobenzene with *o*-nitroaniline at 175° in a closed vessel, or by nitrating 2:4'-dinitrodiphenylamine, dissolved in acetic acid, and in other ways; it crystallises from alcohol or acetic acid in heavy yellow prisms, melts at 183–184°, and is slightly soluble in most organic solvents.

2:4:6:2'-*Tetranitrodiphenylamine* may be obtained by heating picryl chloride with *o*-nitroaniline, in presence of alcohol, in a closed vessel or together with 2:4:2':4'-tetranitrodiphenylamine, by nitrating picrylaniline dissolved in acetic acid. It crystallises in elongated, golden-yellow, prismatic needles, melts at 234°, and is slightly soluble in alcohol, toluene, or acetic acid.

2:4:6:2':4'-*Pentanitrodiphenylamine* is prepared by nitrating picrylaniline, picryl-*p*-nitroaniline, or 2:4:6-trinitro-orange IV, dissolved in acetic acid. It crystallises from toluene in small, yellow prisms, melts at 193–194°, and dissolves in an aqueous solution of sodium carbonate, from which a *sodium* derivative, crystallising in cruciform bundles of red-coloured rods, is obtained. The *ammonium* derivative, similarly obtained, forms hexagonal crystals. The tinctorial power of this pentanitrodiphenylamine is very slight, and in this respect it differs markedly from the hexanitro-derivative.

In addition to the foregoing new substances, the following were prepared by analogous methods: *o*-nitrodiphenylnitrosoamine, *p*-nitrodiphenylnitrosoamine, *o*-nitrodiphenylamine, 4:4'-dinitrodiphenylamine, *op'*-dinitrodiphenylamine (m. p. 217–219°), 2:4:4'-trinitrodiphenylamine, and 2:4:2':4'-tetranitrodiphenylamine. In most cases, the solubilities of these substances for a few organic solvents were determined and are given in the original. T. A. H.

Isomeric Schiff's Bases. OTTO ANSELMINO (*Ber.*, 1905, 38, 3989–3997).—When 6-hydroxy-3-methylbenzaldehyde is mixed with aniline in light petroleum or alcoholic solution, a yellow or a red *anil*, $C_{14}H_{13}ON$, separates, according as the temperature is below or above 32°. The two forms have the same solubility and apparently the same crystalline form; the yellow variety melts at 70°, the red at 74°. The peculiar behaviour observed on heating is dealt with in detail. Both anils give with phenylcarbimide the same *urethane*, $C_{21}H_{18}O_2N_2$, which

crystallises from light petroleum in slender, white needles, and melts at 89.5° . They give also the same *hydrochloride*, melting at 205° . Whether the isomerism of the two anils is to be explained by the Hantzsch-Werner hypothesis or whether it is a chemical isomerism due to the presence of quinquivalent nitrogen and quadrivalent oxygen remains to be investigated.

On condensing 6-hydroxy-3-methylbenzaldehyde with *o*-toluidine or with *p*-toluidine, there is no evidence of the existence of the product in more than one form. 6-Hydroxy-3-methylbenzylidene-*o*-toluidine forms yellow leaflets and melts at 93° . 6-Hydroxy-3-methylbenzylidene-*p*-toluidine forms yellow needles and melts at 106.5° .

6-Hydroxy-3-methylbenzylidene-*p*-chloroaniline, however, forms yellow, glistening plates, and, when heated, becomes more and more red in colour, melting at 154.5° to an orange-red liquid; on cooling, the change of colour takes place in the reverse direction.

6-Hydroxy-4-methylbenzylideneaniline, obtained from aniline and *m*-homosalicylaldehyde, forms thick, greenish-yellow prisms or slender needles, melts at 93° , and can be transformed into a white, crystalline form by cooling its solutions. The peculiar behaviour of this substance on solidification is described in detail.

W. A. D.

Asymmetric Nitrogen. XXI. Activation of Phenylbenzylmethylisobutylammonium Hydroxide. EDGAR WEDEKIND and EMANUEL FRÖHLICH (*Ber.*, 1905, **38**, 3933—3938).—*r*-Phenylbenzylmethylisobutylammonium iodide, $C_{18}H_{24}NI$, is formed by addition of benzyl iodide to methylisobutylaniline, but not of isobutyl iodide to benzylmethylaniline. It crystallises in colourless, hexagonal prisms, decomposes at 130 — 131° , and has solubilities resembling those of phenylbenzylmethylpropylammonium iodide (*Abstr.*, 1905, i, 878). The *r*-bromide, $C_{18}H_{24}NBr$, obtained by mixing molecular amounts of methylisobutylaniline and benzyl bromide, crystallises in microscopic prisms, decomposes at 167° , and is more soluble than the iodide. The *d*-camphorsulphonate, $C_{28}H_{39}O_4NS$, formed from the bromide or iodide and silver *d*-camphorsulphonate in boiling ethyl acetate, crystallises in small rods, melts at 168° , and undergoes little or no resolution when fractionally crystallised from ethyl acetate or methyl formate.

1-Phenylbenzylmethylisobutylammonium *d*-bromocamphorsulphonate, $C_{28}H_{38}O_4NSBr$, is prepared from the *r*-bromide and silver *d*-bromocamphorsulphonate in boiling alcoholic ethyl acetate; on concentration of the solution and addition of ether, the salt crystallises in nodular aggregates, melts at about 165° , is very hygroscopic, and is already partly resolved, as it gives $[\alpha]_D + 45^{\circ}$ and $[M]_D + 256^{\circ}$. On fractional crystallisation from alcoholic ethyl acetate, the salt yields fractions having $[\alpha]_D + 27.72^{\circ}$, 13.55° , 3.93° , and -1.55° , and $[M]_D + 156^{\circ}$, 76.42° , 21.89° , and -8.78° ; the last fraction melts at 165° , and, when treated with potassium iodide in concentrated aqueous solution, forms 1-phenylbenzylmethylisobutylammonium iodide, which decomposes at 130 — 131° , and in absolute alcoholic solution has $[\alpha]_D - 91.59^{\circ}$ and $[M]_D - 349^{\circ}$ at 25° , or in chloroform $[\alpha]_D - 78.29^{\circ}$ and $[M]_D - 298^{\circ}$. The diminished rotation in chloroform solution is due to racemisation, as after one hour it becomes $[\alpha]_D - 66.26^{\circ}$.

G. Y.

Absence of Isomerism in Substituted Ammonium Compounds. HUMPHREY O. JONES (*Proc. Camb. Phil. Soc.*, 1905, 13, 169).—The only stable isomerides of quinquivalent nitrogen compounds are the α - and β -phenylbenzylmethylallylammonium compounds described by Wedekind (*Abstr.*, 1900, i, 155). The author finds that the β -compound is really phenylbenzyltrimethylammonium iodide (*Trans.*, 1903, 83, 1409); an abnormal reaction, therefore, occurs between benzylallylaniline and methyl iodide, in which the allyl iodide is removed. L. M. J.

Derivatives of Phenylcarbamic Acid. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 127—136. Romburgh, *Abstr.*, 1901, i, 201).—The following derivatives of phenylcarbamic acid have been examined crystallographically.

Methyl phenylcarbamate is rhombic [$a:b:c=1.5952:1:1$], and has the sp. gr. 1.251 at 19°. Methyl phenylmethylcarbamate is rhombic [$a:b:c=0.8406:1:0.3320$], and has the sp. gr. 1.296 at 19°. Methyl 4-nitrophenylmethylcarbamate separates from alcohol or benzene in small, delicate needles or flat, monoclinic crystals [$a:b:c=0.6640:1:1$; $\beta=70^\circ 58'$], and has the sp. gr. 1.522 at 14°. Methyl 2:4-dinitrophenylmethylcarbamate is monoclinic [$a:b:c=0.7597:1:1.0875$; $\beta=88^\circ 43\frac{1}{3}'$], and has the sp. gr. 1.506 at 14°. Methyl 2:4:6-trinitrophenylmethylcarbamate occurs in two modifications: the α -modification, which crystallises from alcohol, acetone, or benzene, is monoclinic [$a:b:c=0.5758:1:0.8382$; $\beta=75^\circ 41'$], melts at 118°, has the sp. gr. 1.612 at 19°, and slowly changes into the β -modification, which is deposited sometimes together with the α -modification from alcohol in long, rhombic needles [$a:b:c=0.6596:1:1$]; it melts at 114—118° and has the sp. gr. 1.601 at 19°. Ethyl 2:4-dinitrophenylmethylcarbamate separates from a mixture of benzene and light petroleum in large, colourless, lustrous, monoclinic crystals [$a:b:c=0.6525:1:0.7035$; $\beta=69^\circ 59'$], and has the sp. gr. 1.461 at 19°. Ethyl 2:4:6-trinitrophenylmethylcarbamate crystallises from a mixture of benzene and light petroleum in delicate, flat, sherry-coloured, monoclinic needles [$a:b:c=0.9759:1:0.3929$; $\beta=67^\circ 7'$], and has the sp. gr. 1.471 at 14°.

2:4:6-*Trinitrophenylmethylnitroamine*, $C_6H_2(NO_2)_3 \cdot NMe \cdot NO_2$, formed by the action of fuming nitric acid on 2:4-dinitromethylaniline, melting at 178°, crystallises from a mixture of acetone and benzene in small, strongly-refracting, monoclinic needles [$a:b:c=2.7823:1:3.5242$; $\beta=73^\circ 31\frac{1}{2}'$], melts at 127°, and has the sp. gr. 1.570 at 19°. G. Y.

Constitution of Aromatic Purpuric Acids. VIII. **Picramic Acid and Potassium Cyanide.** WALTHER BORSCHÉ and ARNOLD HEYDE (*Ber.*, 1905, 38, 3938—3942. Compare *Abstr.*, 1900, i, 645; 1902, i, 226; 1904, i, 166, 574; 1905, i, 51, 894).—Picramic acid (2:4-dinitro-6-aminophenol) interacts with potassium cyanide less easily than do the 2:4-dinitrophenols investigated previously, with formation of the potassium derivatives of 2:4-dinitro-6-amino-3-cyanophenol and of 4-nitro-2-amino-6-hydroxylamino-5-cyanophenol in about equal amounts.

Potassium picramopurpurate (potassium 4-nitro-2-amino-6-hydroxy-5-amino-5-cyanophenoxide), $C_7H_5O_4N_4K, H_2O$, forms an almost black, crystalline powder, having a green, metallic lustre, and when treated with phosphoric acid yields the *phenol* as an unstable, dark brown, flocculent precipitate. The *ammonium* salt, $C_7H_5O_4N_4 \cdot NH_4$, prepared by the action of a current of carbon dioxide on the aqueous solution of the potassium salt, covered with ether, and treatment of the dry ethereal solution with ammonia, forms a red, flocculent precipitate.

Potassium 2 : 4-dinitro-6-amino-3-cyanophenoxide, $C_7H_3O_5N_4K$, separates from water or aqueous potassium cyanide solution in dark brown crystals with metallic lustre, decomposes with evolution of nitric oxide when heated, and dissolves in water to form a red solution. The *phenol*, $C_7H_4O_5N_4$, liberated from the potassium salt by an excess of dilute hydrochloric acid, separates from methyl alcohol as a reddish-yellow powder and detonates when heated. The *ammonium* salt forms dark red crystals and decomposes explosively at 150° . When boiled with sodium nitrite and sulphuric acid in aqueous alcoholic solution, 2 : 4-dinitro-6-amino-3-cyanophenol yields 3-hydroxy-2 : 6-dinitrobenzonitrile.

G. Y.

Nitrohalogen Derivatives of Anisole. FRÉDÉRIC REVERDIN and KARL PHILIPP (*Ber.*, 1905, **38**, 3774—3777. Compare Reverdin and Eckhard, *Abstr.*, 1900, i, 28).—2-Chloro-4 : 6-dinitroanisole, formed by the action of nitric acid of sp. gr. 1.52 and concentrated sulphuric acid on *o*-chloro-*p*-nitroanisole, when reduced with tin and hydrochloric acid, yields the *m*-diamine, which condenses with chlorodinitrobenzene in alcoholic sodium acetate solution to form a carmine or yellowish-red, crystalline substance, melting at 182 — 185° .

Nitration of 2-chloro-5-nitroanisole at 19 — 37° leads to the formation of 2-chloro-4 : 5-(or 5 : 6)dinitroanisole, which crystallises in colourless needles, melts at 79° , is easily soluble in the ordinary organic solvents, and, when reduced, yields a substance which gives the *o*-diamine reaction with benzaldehyde and phenanthraquinone.

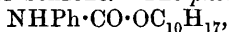
The action of nitric acid of sp. gr. 1.52 and concentrated sulphuric acid on *m*-chloroanisole at -10° to $+20^\circ$ leads to the formation of *m*-chlorodinitroanisole, $C_7H_5O_5N_2Cl$, which crystallises in leaflets and melts at 102 — 104° , whilst the action of nitric acid alone leads to the formation of a *nitro*- or *dinitro*-derivative, which crystallises in white needles and melts at 81° .

When nitrated in concentrated sulphuric acid solution at -10° , *m*-iodoanisole yields *m*-iododinitroanisole, which melts at 102° .

G. Y.

Decahydro- α -naphthol and A-Octahydronaphthalene. HENRI LEROUX (*Compt. rend.*, 1905, **141**, 953—954. Compare *Abstr.*, 1905, i, 278).—Decahydro- α -naphthol, obtained by the direct hydrogenation of α -naphthol below 200° by Sabatier and Senderens' method, crystallises from light petroleum or acetone in colourless needles melting at 62° , boils at 109° under 12 mm. or at 230° under the ordinary pressure, is sparingly soluble in water, readily so in the ordinary solvents, and is volatile in steam. The *acetate*, $C_{10}H_{17} \cdot OAc$, is a colourless liquid with

an agreeable fruity odour, boiling at 127° under 18 mm. pressure; the *benzoate*, $C_{10}H_{17}OBz$, obtained by heating decahydro- α -naphthol with benzoic anhydride in a sealed tube at 175° for twelve hours, crystallises from alcohol in colourless plates melting at 68° and is readily soluble in ether or benzene. The *phenylcarbamate*,



crystallises from alcohol in thin needles melting at 110° .

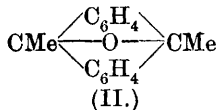
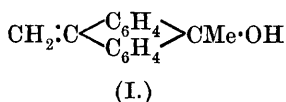
A-Octahydronaphthalene, $C_{10}H_{16}$, obtained by heating decahydro- α -naphthol with phosphoric oxide, anhydrous oxalic oxide, or potassium hydrogen sulphate, differs in the nature of its derivatives from the corresponding compound obtained from decahydro- β -naphthol, which should be designated *B-octahydronaphthalene* (compare Abstr., 1905, i, 278). *A-Octahydronaphthalene* is a colourless liquid boiling at 190 – 191° , having a sp. gr. 0.931 at 0° or 0.914 at 17° , and n_D 1.4993 at 17° ; it unites directly with bromine to form *A-dibromo-octahydronaphthalene*, $C_{10}H_{16}Br_2$, which crystallises from chloroform in colourless prisms, begins to sublime at 120° , and melts at 145° . M. A. W.

γ -Substituted Anthracene Derivatives. Parts II and III.

ALFRED GUYOT and CH. STAEHLING (*Bull. Soc. chim.*, 1905, [iii], 33, 1144–1152, 1152–1161. Compare Abstr., 1905, i, 885).—9:10-*Di-*

hydroxy-9:10-dimethyldihydroanthracene, $C_6H_4 \begin{smallmatrix} \diagup CMe(OH) \\ \diagdown CMe(OH) \end{smallmatrix} C_6H_4$, obtained by the interaction of magnesium methyl iodide with anthraquinone, crystallises from methyl alcohol in large, colourless, transparent prisms, effloresces in air, but retains 1 mol. of the solvent even when dried at 100° under reduced pressure, melts when anhydrous at 181° , and dissolves in sulphuric acid to form a green solution, which slowly becomes yellow. The *dimethyl ether*, prepared by the addition of a small quantity of hydrochloric acid to a solution of the dihydroxy-compound in methyl alcohol, crystallises in needles, melts at 197° , and gives a green coloration with sulphuric acid.

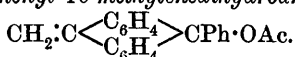
When 9:10-dihydroxy-9:10-dimethyldihydroanthracene, dissolved in acetic acid, is boiled, there is formed a bright yellow, crystalline powder, which melts at about 223° and is slightly soluble in organic solvents. The constitution of this *substance* is considered to be represented by one of the following formulæ, of which (I) is regarded as the more probable:



The *methyl ether* of this dehydration product is formed when the dimethyl ether of 9:10-dihydroxy-9:10-dimethyldihydroanthracene is heated at 100° . It crystallises from a mixture of benzene and methyl alcohol in long, pale straw-coloured needles and is readily soluble in benzene or its homologues, less so in alcohols. When to the dihydroxy-compound, dissolved in acetic acid, a few drops of hydrochloric or sulphuric acid are added, a second dehydration *product* is also formed: this is a yellow, crystalline powder, which melts above 330° , is almost

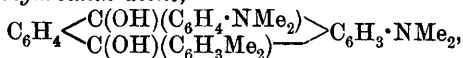
insoluble in organic solvents, and is consequently difficult to purify. Its composition is represented by the formula $C_{36}H_{74}O$.

10-Hydroxy-9-methoxy-9-phenyl-10-methyldihydroanthracene, obtained by the action of magnesium methyl iodide on the methyl ether of phenyl-oxanthranol, crystallises from a mixture of alcohol and benzene in silky, white needles and melts at about 201° . The corresponding *ethoxy*-derivative forms colourless crystals and melts at 176° . Each of these ethers gives a green coloration with sulphuric acid and, when dissolved in acetic acid and boiled for a few minutes, furnishes the dehydration product 9-acetoxy-9-phenyl-10-methylenedihydroanthracene,

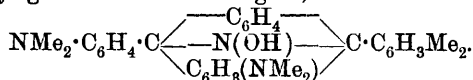


This is a yellow, crystalline substance showing a green fluorescence; it melts at 221° , and when hydrolysed with hydrochloric acid yields 9:10-dihydroxy-9-phenyl-10-methyldihydroanthracene, which forms brilliant yellow crystals melting at 132° . On oxidation with potassium dichromate in acetic acid, the acetyl derivative yields phenyl-oxanthranol and some 9:10-dihydroxy-9-phenyl-10-methyldihydroanthracene.

3-Dimethylamino-9:10-dihydroxy-9-p-dimethylaminophenyl-10-mp-dimethylphenyldihydroanthracene,

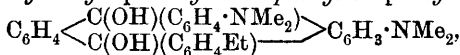


obtained by the condensation of tetramethyldiaminophenyl-oxanthranol with *o*-xylene in presence of sulphuric acid, is a colourless, crystalline powder, melts at 185° , and is readily soluble in benzene or its homologues. Its salts with mineral acids are reddish-brown and dye wool and cotton, mordanted with tannin and tartar emetic, in yellowish-brown tints. It condenses with hydroxylamine to form a compound, which, by analogy with those similarly obtained by Haller and Guyot from phthalyl-green and its homologues, has the constitution



This forms small, white crystals and melts at 246° . With phenylhydrazine, an analogous product is formed which is crystalline and melts at 236° .

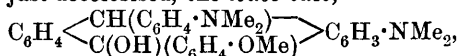
3-Dimethylamino-9:10-dihydroxy-9-p-methylaminophenyl-10-p-ethylphenyldihydroanthracene,



produced by condensing ethylbenzene with tetramethyldiaminophenyl-oxanthranol, is a colourless, crystalline powder and melts at 163° . The condensation product with hydroxylamine, $C_{32}H_{33}ON_3$, forms colourless crystals and melts at 221° ; that with phenylhydrazine, $C_{38}H_{38}N_4$, is yellowish-brown and crystalline and melts at 215° .

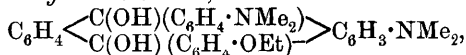
3-Dimethylamino-9:10-dihydroxy-9-p-dimethylaminophenyl-10-p-methoxyphenyldihydroanthracene, similarly obtained from anisole and tetramethyldiaminophenyl-oxanthranol and purified by means of its zinc-chloride, forms small, white crystals and melts at 176° . The hydroxylamine condensation product forms small, white crystals and melts at 203° ; that with phenylhydrazine forms brilliant yellow crystals

containing 1 mol. of the solvent (benzene) and melts at 213°. When a solution of the original base in hydrochloric acid is treated with zinc dust until it is just decolorised, the *leuco-base*,



is formed; this crystallises from a mixture of benzene and alcohol in small, colourless crystals, melts at 246°, and dissolves in acids without producing any coloration.

3-Dimethylamino-9 : 10-dihydroxy-9-p-dimethylaminophenyl-10-p-ethoxyphenyl-9 : 10-dihydroanthracene,



obtained by condensing phenetole with tetramethyldiaminophenyl-oxanthranol and purified by means of the crystalline *zincochloride*, is a colourless, crystalline powder and melts at 175°. Its *condensation product* with hydroxylamine crystallises from benzene in colourless needles and melts at about 208°; that with phenylhydrazine forms brilliant yellow needles and melts at about 186°.

Phenol condenses with tetramethyldiaminophenyl-oxanthranol to form a dihydroxy-derivative of the usual type, which yields a crystalline red *zincochloride*. The base was, however, not obtained pure. The condensation product with pyrogallol yields a *sulphate*, which occurs in carmine-red needles and dyes cotton mordanted with alumina an intense indigo-blue, sensitive to acids and to light. The analogous *product* obtained with catechol behaves similarly, yielding a greener, still more fugitive, blue. In neither of these cases was the free base obtained pure.

T. A. H.

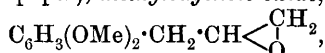
1 : 3 : 6-Trihydroxynaphthalene. RICHARD MEYER and ERNST HARTMANN (*Ber.*, 1905, 38, 3945—3956. Compare Kalle & Co., D.R.-P. 112176, 1899).—1 : 3 : 6-Trihydroxynaphthalene is best prepared on the small scale by fusing sodium 1 : 6-dihydroxynaphthalene-3-sulphonate with three and a third times its weight of sodium hydroxide added in the form of a concentrated solution. After some three hours at 250°, the reaction is complete, and, on the addition of concentrated hydrochloric acid, the crystalline *hydrochloride*, $\text{C}_{10}\text{H}_5(\text{OH})_3 \cdot \text{HCl}(\text{?})$, is obtained in the form of yellow, well-developed needles. The pure hydroxy-derivative is most readily obtained by decomposing the hydrochloride with water; it may be crystallised from hot water if the solution is rapidly cooled, and forms doubly-refracting, cube-shaped crystals, melts at 95°, and is sparingly soluble in benzene, toluene, chloroform, or light petroleum. With ferric chloride, it gives a yellowish-brown precipitate. The *triacetate*, $\text{C}_{10}\text{H}_5(\text{OAc})_3$, crystallises in colourless needles, melts at 112—113°, and is insoluble in alkalis. The *tribenzoate*, $\text{C}_{10}\text{H}_5(\text{O} \cdot \text{COPh})_3$, crystallises from acetone.

A *polymeride*, $\text{C}_{20}\text{H}_{16}\text{O}_6$, probably 2 : 4 : 7 : 3' : 6' : 8'-hexahydroxy-1 : 2-dihydro-2 : 2'-dinaphthyl, $\text{C}_{10}\text{H}_6(\text{OH})_3 \cdot \text{C}_{10}\text{H}_4(\text{OH})_3$, is obtained when an aqueous solution of the trihydroxynaphthalene is boiled for some time, especially in presence of animal charcoal. It crystallises in colourless plates, does not melt, but decomposes at about 304°, and dissolves

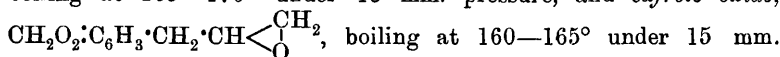
readily in alcohol, ether, or acetone. The solution in sodium hydroxide is yellow, turns red only after several days, and even then is not fluorescent. With ferric chloride, it gives a reddish-brown precipitate. The *acetate*, $C_{20}H_{10}(OAc)_6$, crystallises from water in colourless plates and melts at 200° . The *benzoate*, $C_{20}H_{10}(O\cdot CPh)_6$, forms colourless needles melting at 244° .

Benzeneazo-1:3:6-trihydroxynaphthalene, $C_{10}H_4(OH)_3\cdot N_2Ph$, forms indistinct, microscopic, red needles which dissolve readily in most organic solvents. The polymeride also yields an azo-dye, but this could not be obtained in a crystalline form. No definite products have been obtained by distilling the polymeride with zinc dust. J. J. S.

Some Aromatic Ethylene Oxides. ERNEST FOURNEAU and MARC TIFFENEAU (*Compt. rend.*, 1905, 141, 662—663. Compare Abstr., 1905, i, 523, 591).—In addition to the aromatic monosubstituted ethylene oxides already described, namely, allylbenzene oxide and estragole oxide (the latter boils at 258 — 263° and not at 153 — 156° as stated in the original paper), *methyleugenole oxide*,



boiling at 165 — 170° under 15 mm. pressure, and *safrrole oxide*,



pressure, have been prepared. These oxides are partially decomposed on heating into the isomeric aldehydes, dihydrocinnamaldehyde, *p*-methoxydihydrocinnamaldehyde, dimethoxydihydrocinnamaldehyde, and methylenedioxydihydrocinnamaldehyde respectively. Symmetrical

disubstituted ethylene oxides of the type $\begin{array}{c} CHR \\ | \\ CHMe \end{array} \begin{array}{c} \text{---} \\ \diagup \end{array} O$, where R represents an aromatic radicle, are converted into the isomeric ketones on distillation, thus methylisoeugenole oxide yields dimethoxyphenylacetone (compare Höring, Abstr., 1905, i, 592). Asymmetrical disubstituted

ethylene oxides of the type $\begin{array}{c} CRMe \\ | \\ CH_2 \end{array} \begin{array}{c} \text{---} \\ \diagup \end{array} O$ are readily converted by heating into the corresponding aldehyde, $CHRMe\cdot CHO$ (compare Behal and Tiffeneau, Abstr., 1905, i, 883). M. A. W.

Presence of Lupeol in some kinds of Gutta-percha. PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 137).—The alcohol melting at 210° , obtained on hydrolysis of Tschirch's crystalalban (Abstr., 1904, i, 76, 905), is identical with lupeol (Schulze, Abstr., 1904, i, 582). It is obtained in the form of its acetate from djelutung, the product of the milky juice of some species of *Dyera*, which is related to gutta-percha and is known commercially as bresk or pontianak. On oxidation with chromic acid, it yields a crystalline ketone which melts at 169° and forms a crystalline product with hydroxylamine.

Djelutung yields also an acetic ester which melts at 238° ; this has been isolated previously from the gutta-percha of *Payena Leerii*, and on hydrolysis yields an alcohol melting at 195° . G. Y.

Nitro-*m*-toluic Acids. WALDEMAR FINDEKLEE (*Ber.*, 1905, **38**, 3553—3558).—Contrary to the statement in *Beilstein's Handbuch* that 4-nitro-*m*-toluic acid melts at 219° and yields an amino-acid melting at 172°, the author shows that the acid possessing these constants is the 2-nitro-acid, whilst the 4-acid melts at 134° and yields an amino-acid melting at 175°. The 4-nitro-acid yields a white, insoluble silver salt; the *amide*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO} \cdot \text{NH}_2$ [4 : 1 : 3], separates from alcohol in stout, flat needles and melts at 176—177°. The 4-amino-acid yields an amide, $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO} \cdot \text{NH}_2$ [4 : 1 : 3], melting at 179°. The 2-amino-acid, which is formed as a by-product in the action of nitric acid on *m*-toluic acid, condenses with formamide to form 8-methylquinazoline, $\text{C}_6\text{H}_3\text{Me} \cdot \begin{smallmatrix} \text{N}=\text{CH} \\ \text{CO} \cdot \text{NH} \end{smallmatrix}$, which separates from alcohol in needles, melts at 251°, and gives a crystalline *platinichloride* and *chromate*. T. M. L.

Cinnamic Acid from Storax. EMIL ERLÉNMEYER, jun. (*Ber.*, 1905, **38**, 3891—3892. Compare *Abstr.*, 1905, i, 892).—Cinnamic acid from storax gave a quantitative yield of the brucine salt melting at 135°, and no trace of the salt of lower melting point. In 1 per cent. solution, the salt gave no rotation, but showed a dextro-rotation in a 5 per cent. solution. It is suggested that the synthetical acid contains a racemic modification, produced during saponification with sodium hydroxide. T. M. L.

Syntheses of Carboxylic Acids. II. JOSEF HOUBEN (*Ber.*, 1905, **38**, 3796—3801. Compare *Abstr.*, 1903, i, 825; Houben and Kesselkaul, *Abstr.*, 1903, i, 42).—On addition of traces of methyl iodide to a mixture of 1 mol. of dibromobenzene and 1 mol. of powdered magnesium in ethereal solution, a violent reaction takes place, which must be moderated by cooling with ice and concentrated sulphuric acid; the action of anhydrous carbon dioxide on the product and subsequent decomposition with ice and dilute hydrochloric acid leads to the formation of small quantities of *p*-bromobenzoic and terephthalic acids, together with traces of 4:4'-dibromoacetophenone (compare Bodroux, *Abstr.*, 1904, i, 64; Jocitsch, *Chem. Zeit.*, 1903, **27**, 56).

4-Bromo-*α*-naphthoic acid, obtained in the same manner from 1:4-dibromonaphthalene in a yield of 20 per cent. of the theoretical, sublimes in small, colourless, glistening crystals and melts at 204—209°. It could not be obtained in a state of purity.

Dihydropinenecarboxylic acid, formed from pinene hydrochloride (Houben and Kesselkaul, *loc. cit.*), crystallises in prisms, melts at 72—74°, and boils at 153° under 13 mm. or at 268° under the atmospheric pressure. The *sodium* salt forms colourless leaflets; the *silver* salt is obtained as a white precipitate, sensitive to light. The *anhydride*, $\text{C}_{22}\text{H}_{34}\text{O}_3$, formed by boiling the acid with acetyl chloride, crystallises from alcohol in glistening, silky threads and melts at 211—212°. Together with the carboxylic acid, pinene hydrochloride yields borneol, and Étard and Meker's dicamphene hydride.

The action of magnesium and carbon dioxide on bornyl chloride leads to the formation of an acid which melts at 72° (compare Zelinsky, *Abstr.*, 1903, i, 185). G. Y.

Acid Function of Aromatic Hydroxyl. ALFRED THIEL, A. SCHUMACHER, and HERMANN ROEMER (*Ber.*, 1905, **38**, 3860—3862).—The basicity of aromatic hydroxylic compounds can be determined even more effectively by conductivity measurements than by titration with sensitive indicators. Using this method, it is found that orcyaldehyde is dibasic and gives coloured alkaline solutions; orsellin acid behaves similarly, but paraorsellin acid (orcincarboxylic acid) is monobasic and yields colourless alkali salts. This result is in accord with the view that in the latter compound both hydroxyls are in ortho-positions relatively to the carboxyl, whilst in the former acid only one hydroxyl is in the ortho-position to the carboxyl group.

T. M. L.

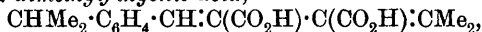
Butadiene Compounds. IX. Yellow Monoarylfulgides. HANS STOBBE (*Ber.*, 1905, **38**, 3893—3897. Compare Abstr., 1905, i, 857).—[With ALFRED LENZNER.]—*δ*-Phenyl-*αα*-dimethylfulgenic acid, $\text{CMe}_2\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CHPh}$, prepared from benzaldehyde and ethyltetraconate, crystallises from 80 per cent. acetic acid in irregular, colourless prisms and softens and melts at 213—214°, decomposing and becoming yellow. Acetyl chloride converts it into a yellow and a white fulgide, $\text{CHPh}\cdot\text{C}\cdot\text{CO} > \text{O}$; both melt at 115—116° and crystallise in rhombohedra; in sunlight, the yellow form becomes lighter, the white form becomes yellow, and when recrystallised both forms again separate. From a supersaturated solution of the yellow form, a yellow crystal brings down only the yellow form, a white crystal a mixture; so, conversely, with the white form.

[With EMIL WAHL.]—*δ*-*p*-Tolyl *αα*-dimethylfulgenic acid, $\text{CMe}_2\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Me}$, prepared from *p*-tolualdehyde and ethyl dimethylitaconate, crystallises from 50 per cent. acetic acid and melts at 224°. The fulgide, $\text{C}_{15}\text{H}_{14}\text{O}_3$, crystallises from light petroleum in pointed, yellow prisms and melts at 107°.

T. M. L.

Butadiene-compounds. X. Two Cumyldimethylfulgenic Acids and a Third Isomeride. HANS STOBBE and KARL LEUNER (*Ber.* 1905, **38**, 3897—3903).—Two stereoisomeric fulgenic acids are produced by the condensation of cuminaldehyde with ethyl tetraconate.

δ-Cumyl-*αα*-dimethylfulgenic acid,



the main product, separates from 80 per cent. acetic acid in microscopic crystals, softens at 215°, and melts at 225°, liberating gas and becoming yellow. The barium salt, $\text{C}_{17}\text{H}_{18}\text{O}_4\text{Ba}\cdot 2\text{H}_2\text{O}$, forms a flocculent precipitate, loses H_2O at 150° and the second molecule at 170°. The fulgide, $\text{C}_{17}\text{H}_{18}\text{O}_3$, of normal molecular weight, crystallises from light petroleum in yellow, sharp-edged forms of the colour of monoclinic sulphur and melts at 85°. When a solution in benzene containing iodine is exposed to light, it is for the most part converted into the stereoisomeride.

The *allo*-acid crystallises from dilute acetic acid in small, six-sided tablets, begins to melt at 200°, and decomposes vigorously at 208°.

The *allo-fulgide* separates from light petroleum in long prisms and melts at 112° .

Both acids are reduced by sodium amalgam to a *dihydro-acid*, $C_{17}H_{22}O_4$, which melts at $135-137^{\circ}$. This and the two preceding acids, when oxidised, yield cuminaldehyde, acetone, and oxalic acid.

A third acid found in the interaction was shown to be *α-cumylidene-δδ-dimethylparaconic acid*, $C_3H_7 \cdot C_6H_4 \cdot CH : C \begin{array}{c} \text{CH}(\text{CO}_2H) \\ \text{CO} \end{array} \text{CME}_2$; the acid softens and melts at 192° without decomposing. T. M. L.

Hydroxydiphenic Acids. JULIUS SCHMIDT and RICHARD SCHALL (*Ber.*, 1905, 38, 3769—3774).—4-Amino- and 4:4'-diamino-diphenic acids may be readily diazotised, and when the solutions of the diazonium salts are heated, the corresponding hydroxy-acids are obtained. 4-Hydroxydiphenic acid crystallises in yellow prisms, melts at $245-246^{\circ}$, dissolves readily in alcohol, ether, or water, but only sparingly in benzene. 4:4'-Dihydroxydiphenic acid, $C_{14}H_{10}O_6 \cdot H_2O$, crystallises in pale yellow prisms, melting and decomposing at $272-273^{\circ}$. Silver and barium salts have been prepared. The diacetyl derivative, $C_{12}H_6(\text{OAc})_2(\text{CO}_2H)_2$, crystallises in colourless needles and melts and decomposes at $222-223^{\circ}$.

When 6:6'-diaminodiphenic acid is diazotised and the solution heated, 6-amino-6'-hydroxydiphenic acid, $NH_2 \cdot C_{12}H_6(\text{CO}_2H)_2 \cdot OH$, is produced. It forms yellow, microscopic needles which melt and decompose at $312-313^{\circ}$. It dissolves only sparingly in the usual organic solvents. The formation of an aminohydroxy- and not of a dihydroxy-acid is attributed to stereochemical causes.

The acids are not esterified by the usual catalytic methods. Full directions for the preparation of the two diamino-acids are given (compare Schmidt and Kämpf, *Abstr.*, 1904, i, 70 and 71). J. J. S.

Constitution of Fluorescein. EMILIO NOELTING (*Ber.*, 1905, 38, 4023).—The author in a recent paper (*Abstr.*, 1905, i, 935) had overlooked the work of R. Meyer (*Abstr.*, 1895, i, 291, 538; 1897, i, 69). W. A. D.

Mutual Exchange of Aromatic Complexes. RICHARD MEYER and HERMANN PFOTENHAUER (*Ber.*, 1905, 38, 3958—3963).—Fluorescein is formed when phenolphthalein and resorcinol are heated in an oil-bath at $180-200^{\circ}$ during some forty-eight hours. The reaction is not complete even when a large excess of resorcinol is used. The fluorescein was characterised by conversion into eosin.

Catecholphthalein is completely transformed into fluorescein when heated at $210-220^{\circ}$ with five times its weight of resorcinol. Quinol-phthalein is not decomposed when heated with resorcinol and fluorescein is not decomposed when heated with phenol. J. J. S.

Thio-compounds prepared from Ketones and Aldehydes. COMPAGNIE MORANA (D.R.-P. 162059).—Ketones and aldehydes react with aqueous solutions of alkali sulphides or polysulphides, the ketonic oxygen being replaced by sulphur, and condensation of the

aldehyde group taking place at the same time, water being eliminated. Thus, acetophenone and formaldehyde yield a *compound*, C_9H_8S [$?CH_2:CH:CSPh$], which separates as a viscous, yellow oil and boils with partial decomposition at $130-140^\circ$ under 20 mm. pressure. It is insoluble in water, ether, or light petroleum, sparingly soluble in alcohol, readily so in benzene, and does not distil in a current of steam.

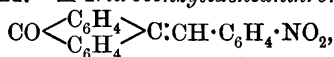
Benzophenone, formaldehyde, and alkali sulphides yield a *compound*, $C_{13}H_{10}S$, which crystallises in white needles, melts at 36° , and dissolves readily in alcohol. Acetone and citral yield a *compound*, $C_{13}H_{20}S$, which forms a yellow oil with a faint odour of leeks, and boils at $150-153^\circ$ under 12 mm. pressure.

C. H. D.

Benzylidene Derivatives of Anthrone or Anthranol. ALBIN HALLER and PADOVA (*Compt. rend.*, 1905, 141, 857—861).—Liebermann's anthranol, $C_6H_4<\begin{smallmatrix} C(OH) \\ CH \end{smallmatrix}>C_6H_4$ (compare Abstr., 1882, 855 ;

1887, 965), reacts in alkaline medium as its tautomeride, anthrone, $CO<\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}>CH_2$ (compare Goldmann, Abstr., 1888, 714, 1202 ; Thörner and Zincke, Abstr., 1878, 231), condensing with aromatic aldehydes to form compounds of the type $CO<\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}>C:CHR$.

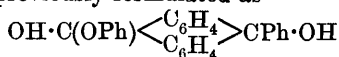
Benzylideneanthrone, $CO<\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}>C:CHPh$, prepared by heating anthranol and benzaldehyde in pyridine solution containing a little piperidine, forms yellow needles melting at $126-127^\circ$ (compare Levi, Abstr., 1885, 1240 ; Bach, Abstr., 1890, 1144, 1425), and can also be prepared by dehydrating, by means of hydrogen chloride, benzyloxanthranol, $CO<\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}>C(CH_2Ph) \cdot OH$, obtained from anthraquinone and magnesium benzyl chloride (compare Haller and Guyot, Abstr., 1904, i, 314). *Anisylideneanthrone* (p-methoxybenzylideneanthrone), $CO<\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}>C:CH \cdot C_6H_4 \cdot OMe$, crystallises from alcohol or acetic acid in long, yellow needles, melting at $140.5-141.5^\circ$, and is less soluble in alcohol, acetic acid, ethyl acetate, chloroform, or benzene than the benzylidene compound. *m-Nitrobenzylideneanthrone*,



melts at $165.5-166.5^\circ$, is readily soluble in chloroform, benzene, acetic acid, or pyridine, slightly so in methyl or ethyl alcohol, and insoluble in light petroleum.

M. A. W.

meso-Phenylated Derivatives of Anthracene. A Correction. CARL LIEBERMANN and SIMON LINDENBAUM (*Ber.*, 1905, 38, 3802—3804).—The compound previously formulated as



and its monoacetyl derivative (Abstr., 1905, i, 522) are shown to be

9-hydroxyphenyl-9-phenylanthrone, $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CPh} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, and its acetyl derivative.

T. M. L.

Phenanthrene Derivatives. XVII. Conversion of 4:5-Dinitrophenanthraquinone into 4:5-Aminohydroxyphenanthraquinone. JULIUS SCHMIDT and FRITZ LEIPPRAND (*Ber.*, 1905, **38**, 3733—3737. Compare Abstr., 1901, i, 76, 464; 1902, i, 29, 715, 757, 797; 1903, i, 557, 691; 1904, i, 69, 70, 71, 1033, 1034).—4:5-Dinitrophenanthraquinone (Abstr., 1904, i, 71) is readily reduced by stannous chloride at 30° in the presence of hydrochloric and acetic acids to the *hydrochloride* of 4-nitro-5-aminophenanthraquinol, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{C} \cdot \text{OH}$ $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{C} \cdot \text{OH}$, which forms yellowish-red crystals readily soluble in water. 4-Nitro-5-aminophenanthraquinone is formed as a dark brown powder when a current of air is passed through a paste of the hydrochloride and saturated sodium carbonate solution; it decomposes when slowly heated, and dissolves but sparingly in most organic solvents. The *diacetyl* derivative, $\text{N} \cdot \text{Ac}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CO}$ $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CO}$, crystallises in dark brown needles and melts at 280°.

4-Nitro-5-hydroxyphenanthraquinone is obtained when the corresponding nitroamino-compound is diazotised and the clear solution of the diazonium salt heated on the water-bath. It is a reddish-brown powder, melts and decomposes at 240°, and dissolves readily in alcohol, ether, or ethyl acetate to deep red solutions. It also dissolves in concentrated sulphuric acid and in alkalis, and has such pronounced acidic properties that it can be completely removed from its ethereal solutions by shaking with sodium carbonate solution. The *acetyl* derivative, $\text{O} \cdot \text{Ac} \cdot \text{C}_6\text{H}_3 \cdot \text{CO}$ $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CO}$, crystallises in yellowish-green needles; when heated, it sinters at 200° and melts and decomposes at 220°.

4-Amino-5-hydroxyphenanthraquinone is obtained by reducing the nitroamino-compound to aminohydroxyphenanthraquinol hydrochloride, and then decomposing this with sodium carbonate in presence of atmospheric oxygen. It forms a black powder and dissolves sparingly in the usual organic solvents.

J. J. S.

Phenanthrene Derivatives. XVIII. Conversion of Phenanthrene into Fluorene Compounds. JULIUS SCHMIDT and KARL BAUER (*Ber.*, 1905, **38**, 3737—3757. Compare Anschütz and Schultz, *Annalen*, 1879, **196**, 50; R. Meyer and Spengler, Abstr., 1905, i, 219).—The 2-nitro-, 4-nitro-, 2:7-dinitro-, 4:5-dinitro-, 2-bromo-, 2:7-dibromo-, and 2:7-bromonitro-derivatives of phenanthraquinone, when heated with aqueous 10 per cent. sodium or potassium hydroxides, are converted into the corresponding derivatives of 9-hydroxyfluorene-9-carboxylic acid, and when these are heated with acetic anhydride in the atmosphere of hydrogen they lose carbon dioxide and yield derivatives of fluorenyl acetate, $\text{C}_6\text{H}_4 > \text{CH} \cdot \text{O} \cdot \text{Ac}$.

When boiled with acetic anhydride, with water, or with alkalis in the presence of air, they yield derivatives of fluorenone.

The nature of the substituents in the phenanthraquinone molecule affects the transformation; thus, with 10 per cent. potassium hydroxide, phenanthraquinone itself requires a temperature of 80° , and the mononitro-derivatives of from 50 — 65° , whilst the dinitro-derivatives are transformed at 15° . Bromine substituents also facilitate the transformation, but not to the same extent.

The stability of the hydroxyfluorene-carboxylic acids is diminished by the presence of nitro-groups.

2-Nitro-9-hydroxyfluorene-9-carboxylic acid, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 > \text{C} \begin{matrix} \text{OH} \\ \text{CO}_2\text{H} \end{matrix}$, C_6H_4

forms yellowish-brown prisms, melts and decomposes at 160 — 161° , and is decomposed when boiled with water. It dissolves readily in ether, chloroform, or benzene, and all solutions are coloured brown.

2-Nitrofluorenyl acetate, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 > \text{CH} \cdot \text{OAc}$, C_6H_4 crystallises from acetic acid in yellow needles melting at 155 — 156° , and when boiled with concentrated hydrochloric acid yields a compound melting at 129 — 130° .

4-Nitro-9-hydroxyfluorene-9-carboxylic acid crystallises in colourless needles, melts at 156 — 158° , may be crystallised quickly from hot water, and is only sparingly soluble in benzene or chloroform. The solution in *N*/10 sodium hydroxide yields characteristic precipitates with silver nitrate, lead acetate, and cupric sulphate. *4-Nitrofluorenyl acetate* crystallises from alcohol in colourless plates, melts at 112 — 113° , and is readily soluble in the usual organic solvents. When hydrolysed with concentrated hydrochloric acid, it yields a compound, $\text{C}_{13}\text{H}_9\text{O}_4\text{N}$, melting at 105 — 107° . *4-Nitrofluorenone*, $\text{C}_{13}\text{H}_7\text{O}_3\text{N}$, is obtained together with the compound $\text{C}_{26}\text{H}_{14}\text{O}_3\text{N}_2$ when the carboxylic acid is boiled with water. It crystallises from acetic acid, in which it is moderately soluble, and melts at 173 — 174° . Its *oxime*, $\text{C}_{13}\text{H}_8\text{O}_3\text{N}_2$, crystallises in dark green needles which melt and decompose at 255 — 256° . The *semicarbazone* forms a brown powder, which is not molten at 350° .

2:7-Dinitro-9-hydroxyfluorene-9-carboxylic acid is formed together with *2:7-dinitrophenanthraquinhydrone* when *2:7-dinitrophenanthraquinone* (5 grams) is treated with 10 per cent. potassium hydroxide for fifteen minutes at the ordinary temperature, and then immediately acidified with ice-cold dilute sulphuric acid. The acid crystallises in colourless needles, turns brown at 130° , and melts and decomposes at about 280° . It has a bitter taste and dissolves readily in ethyl alcohol or acetone. *2:7-Dinitrofluorenyl acetate* crystallises in colourless needles, melts at 244° , and decomposes at 247° ; the corresponding

alcohol, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 > \text{CH} \cdot \text{OH}$, $\text{NO}_2 \cdot \text{C}_6\text{H}_3$ forms colourless needles, melts at 212° , and is readily oxidised to *2:7-dinitrofluorenone*, which crystallises from glacial acetic acid in yellow needles melting at 290° . It is identical with Schultz' dinitrofluorenone (Abstr., 1880, 814). The *oxime* melts and decomposes at 285 — 286° , the *phenylhydrazone*

crystallises in dark red, glistening prisms which melt and decompose at 263—264° (compare Abstr., 1896, i, 174), the *semicarbazone* crystallises in pale yellow needles and is not molten at 350°.

4:5-Dinitro-9-hydroxyfluorene-9-carboxylic acid forms brownish-yellow needles, melts and decomposes at 140°, and is moderately soluble in ether, alcohol, or chloroform, and readily in acetone.

4:5-Dinitrofluorenyl acetate forms colourless needles melting at 220—221°; the corresponding alcohol melts at 201—202°, and 4:5-dinitrofluorenone crystallises in yellow needles; these change colour at 330°, but are still solid at 350°. The *oxime* melts at 267—268°, the *phenylhydrazone* melts and decomposes at 241°, and the *semicarbazone* at 288°.

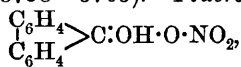
2-Bromo-9-hydroxyfluorene-9-carboxylic acid forms colourless needles, melts and decomposes at 213°, and is only sparingly soluble in benzene. 2-Bromofluorenyl acetate melts at 70—72° and dissolves readily in the usual solvents. 2-Bromofluorenyl alcohol melts at 100—102°. 2-Bromofluorenone, $C_{13}H_7OBr$, crystallises from acetic acid in yellow needles and melts at 134°. The *oxime* melts at 194—195°, the *phenylhydrazone* crystallises in brick-red needles and melts at 148°, the *semicarbazone* melts at about 235°.

2:7-Dibromo-9-hydroxyfluorene-9-carboxylic acid forms white needles and melts and decomposes at 280°. 2:7-Dibromofluorenone is identical with Holm's dibromofluorenone (Abstr., 1883, 921; Werner, 1904, i, 863). The *oxime*, $C_{13}H_7ONBr_2$, crystallises in pale yellow needles and melts and decomposes at 235°, the *phenylhydrazone* forms orange-red needles and melts at 192—193° (compare Abstr., 1896, i, 174), and the *semicarbazone* begins to decompose at 240°, but is still solid at 350°.

2-Bromo-7-nitro-9-hydroxyfluorene-9-carboxylic acid forms a reddish-brown powder and begins to decompose at 160°. 2-Bromo-7-nitrofluorenone forms yellow needles and melts at 230°; it can also be obtained by nitrating 2-bromofluorenone. The *oxime*, $C_{13}H_7O_3N_2Br$, melts and decomposes at 249°, the *phenylhydrazone* forms red needles and melts and decomposes at 245°, the *semicarbazone* is still solid at 350°.

When 9-hydroxyfluorene-9-carboxylic acid is heated for an hour with acetic anhydride on the water-bath, it yields an *isomeride* melting at 212°, and less readily soluble in the ordinary solvents. J. J. S.

Action of Nitric Acid on Fluorenone, and Derivatives of the Nitro-compounds thus obtained. JULIUS SCHMIDT and KARL BAUER (*Ber.*, 1905, 38, 3758—3763).—*Fluorenone nitrate*,

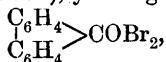


is formed by the action of an excess of concentrated nitric acid of sp. gr. 1.45 on fluorenone at 0°. It is unstable and on exposure to the atmosphere liberates nitric acid. 2:7-Dinitrofluorenone (Schultz, Abstr., 1880, 814) is obtained by boiling the ketone with fuming nitric acid of sp. gr. 1.52.

2:6:7-Trinitrofluorenone is obtained when the ketone is boiled for two hours with a mixture of fuming nitric acid and concentrated sulphuric acid. It crystallises from glacial acetic acid in pale yellow,

glistening needles, melts at 180—181°, and dissolves readily in most organic solvents. Its constitution follows from the fact that when oxidised it yields 3:4-dinitrobenzoic acid and that it may be prepared by further nitration of the 2:7-dinitro-derivative. The *oxime*, $C_{13}H_6O_7N_4$, crystallises from alcohol in practically colourless needles and melts and decomposes at 260°. The *phenylhydrazone* forms glistening, violet plates and melts and decomposes at 276°. The *semicarbazone* melts and decomposes at 299°. When reduced with tin and hydrochloric acid, the trinitro-derivative yields 2:6:7-*triamino-fluorenyl alcohol*, which is extremely unstable. The *hydrochloride*, $C_{13}H_{16}ON_3Cl_3$, is readily soluble in water but insoluble in alcohol. The *picrate* begins to decompose at 175°. 2:6:7-*Triaminofluorenone*, $C_{13}H_{11}ON_3$, melts and decomposes at 198° and is extremely unstable. The *hydrochloride* forms black plates. J. J. S.

Action of Bromine on Fluorene and on Fluorenone. JULIUS SCHMIDT and KARL BAUER (*Ber.*, 1905, **38**, 3764—3768. Compare Fittig and Schmitz, *Abstr.*, 1879, i, 174).—Fittig and Schmitz' β -dibromofluorene is the 2:7-derivative, as it yields on oxidation 2:7-dibromofluorenone (this vol., i, 27). When fluorene is brominated in direct sunlight in chloroform solution, the chief product is 2:6(?) : 7-*tribromofluorene*, which crystallises from alcohol in stout needles melting at 200°. When oxidised, it yields a tribromofluorenone identical with the product obtained by brominating 2:7-dibromofluorenone. Fluorenone unites with bromine in much the same manner as phenanthraquinone (*Abstr.*, 1904, i, 1033), yielding the *dibromide*,



which, however, has not been obtained in a pure state. When heated with bromine water, fluorenone at 100° yields 2-bromofluorenone, or, at 150°, 2:7-dibromofluorenone (*loc. cit.*). 2:6(?) : 7-*Tribromofluorenone*, obtained by heating the 2:7-dibromo-derivative with bromine and water at 160—170°, crystallises from glacial acetic acid in yellow needles melting at 180—181°. The *oxime*, $C_{13}H_6ONBr_3$, melts and decomposes at 243°, the *phenylhydrazone* at 227°, and the *semicarbazone* forms pale yellow needles which are still solid at 350°. J. J. S.

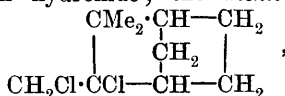
Preparation of Camphor from *iso*Borneol. CHEMISCHE FABRIK AUF AKTIEN FORM. E. SCHERING (D.R.-P. 161523. Compare *Abstr.*, 1905, i, 709).—Oxygen or atmospheric air may be used to oxidise *isoborneol* to camphor. Thus, when *isoborneol* is heated at 160° and volatilised in a current of oxygen, the vapour being led over copper gauze spirals at 180°, the product contains about 20 per cent. of camphor. Air may be employed instead of oxygen, the temperature of the liquid then being 175°. C. H. D.

Action of Hypochlorous Acid on Camphene. KAZIMIR SŁAWIŃSKI (*Bull. Acad. Sci. Cracow*, 1905, 491—500).—The action of

hypochlorous acid on camphene leads to the formation of camphene dichloride and camphene chlorohydrin, which are solid, and a mixture of three liquid chlorocamphenes, $C_{10}H_{15}Cl$.

Camphene chlorohydrin,
$$\begin{array}{c} CMe_2-CH-CH_2 \\ | \quad | \\ CH_2Cl \cdot C(OH) \cdot CH-CH_2 \end{array}$$
, is isolated from

its mixture with the dichloride, than which it is more soluble in methyl alcohol, in the form of its *acetate*, which is obtained also by the action of silver acetate on the dichloride. It melts at 52.5° , and on hydrolysis yields the *anhydride*, $C_{10}H_{16}O$, which is formed also when the mixture of dichloride and chlorohydrin is boiled with aqueous potassium hydroxide; the *dichloride*,



which melts at $139-140^\circ$, remaining unchanged. The anhydride boils at $99-100.5^\circ$ under 20 mm. pressure, has the sp. gr. 0.9372 at $0^\circ/0^\circ$ or 0.9254 at $15^\circ/0^\circ$, and forms a crystalline *additive* compound with sodium hydrogen sulphite, which, on hydrolysis, yields *isocamphenilanaldehyde*, $C_{10}H_{16}O$. This boils, in an atmosphere of hydrogen, at $82-84^\circ$ under 12 mm. pressure, has the sp. gr. 0.9571 at $0^\circ/0^\circ$, or 0.9284 at $15^\circ/0^\circ$, and, when distilled in air, is oxidised to *isocamphenilanic acid* melting at 118° . The aldehyde is probably a stereoisomeride of camphenilanaldehyde (Bredt and Jagelki, Abstr., 1900, i, 134).

The mixture of liquid chloro-compounds contains *chlorocamphene*,

$$\begin{array}{c} CMe_2 \cdot CH-CH_2 \\ | \quad | \\ CHCl : C-CH-CH_2 \end{array}$$
, *chlorocyclene*,
$$\begin{array}{c} CH_2-CMe \cdot CH-CH_2 \\ | \quad | \\ CH_2Cl \cdot C-CH-CH_2 \end{array}$$
, and a

chloro-compound, $C_{10}H_{15}Cl$, which is not a derivative of camphene. On reduction with sodium and alcohol, the mixture of chloro-compounds yields camphene and cyclene, a portion remaining unreduced. When oxidised with potassium permanganate, the mixture yields camphenilone, melting at 38° , traces of a neutral *product*, melting at 205° , dehydrocamphenilic acid, melting at 150.5° , camphenilic acid, melting at 172° , and a small quantity of a liquid acid. The chloro-compound, remaining unoxidised, has the sp. gr. 1.0498 at $0^\circ/0^\circ$ or 1.347 [$\frac{1}{2}$ 1.0347] at $17^\circ/0^\circ$, and does not react with alcoholic silver nitrate.

The action of sodium acetate on the mixture of chloro-compounds, at 140° , leads to the elimination of the one-third of the mixture which interacts with silver nitrate, by formation of an *acetate*, which boils at $106-110^\circ$ under 13 mm. pressure, and on hydrolysis yields a mixture of *alcohols*, $C_{10}H_{16}O$, melting at $45-50^\circ$; on oxidation with potassium permanganate, this forms two neutral substances, melting at $205-207^\circ$ and 150° , respectively, traces of dehydrocamphenilic acid, and a liquid acid. The chloro-compounds remaining after treatment of the mixture with sodium acetate are converted into the acetate of camphene chlorohydrin by the action of acetic and sulphuric acids.

The camphene obtained from isoborneol consists of a mixture of true camphene, cyclene, and the hydrocarbon, which corresponds with camphenocamphoric acid. G. Y.

Caoutchouc. Relations existing between the Hydrocarbons from Caoutchouc and Gutta-percha. CARL D. HARRIES (*Ber.*, 1905, 38, 3985—3989).—The hydrocarbon, $C_{10}H_{16}$, of gutta-percha (compare Tschirch and Müller, *Abstr.*, 1905, i, 452), when subjected to the action of ozone in chloroform solution (compare Harries, *Abstr.*, 1904, i, 757; 1905, i, 364), gives an ozonide, $C_{10}H_{16}O_6$, which resembles the ozonide derived from caoutchouc in giving a mixture of lævulin-aldehyde and lævulic acid when decomposed by steam; the proportions of these two substances are, however, reversed. The opinion is expressed that the fundamental hydrocarbons, $C_{10}H_{16}$, of caoutchouc and gutta-percha are actually identical, both being probably 1:5-dimethylcycloocto- $\Delta^{1:5}$ -diene, and that the ozonides are stereoisomeric derivatives of this hydrocarbon. Provisional formulæ are suggested. W. A. D.

New Fossil Copal (Java Copal). KARL DIETERICH (*Chem. Centr.*, 1905, ii, 1430—1431; from *Pharm. Post.*, 38, 551—553).—A sample of a Java fossil copal consisted of pieces about the size of a walnut which had a turbid or milky appearance, and when ground formed a brownish-grey powder. The copal contained fragments of pyrites and carbon, and had a lustrous, conchoidal fracture; it was as hard as rock salt and had a sp. gr. 1.033—1.041. When heated, it sintered at 160—170°, began to melt at 175°, and formed a clear liquid at 178°. The copal lost 0.265 per cent. at 100°, and yielded 2.44 per cent. of ash, which consisted mainly of ferric oxide; it had an acid number 4.55—5.07, saponification number 14.54—18.03, ester number 9.98—12.96, and Hübl-Waller iodine number 50.86—54.66, but did not contain nitrogen, volatile acids, ethereal oils, or bitter principles. 82.58 per cent. of the copal was insoluble in 96 per cent. alcohol, 41.63 in ether, 80.61 in acetone, 2.59 in chloroform, 3.92 in benzene, 5.84 in carbon disulphide, 92.97 in wood spirit, 2.24 in light petroleum, 95.29 in a 60 per cent., and 90.76 in an 80 per cent. solution of chloral hydrate, 73.36 in dichlorohydrin, 53.96 in epichlorohydrin, and 2.58 in oil of turpentine. When submitted to dry distillation, it did not form a sublimate, and when heated to 120° it yielded 1.07 per cent. of a thin, bright yellow oil together with white vapours, which escaped condensation. The oil contained water and had an odour similar to that of turpentine; it had n_D 1.4803 at 17.5° and 1.4812 at 17°. On raising the temperature to 280°, 15.67 per cent. of a brownish-yellow, highly refractive oil was obtained which had an empyreumatic odour, a sp. gr. 0.921 at 15°, n_D 1.5116 at 17°, and iodine number 87.24—96.53. The third fraction, which distilled at 280—300°, consisted of 22.61 per cent. of a dark oil, which had an empyreumatic odour, remarkably similar to that of oil of wormwood; it had a sp. gr. 0.928 at 15°, and iodine number 113.48—120.74. The presence of tannacetone could not be detected. When the temperature was further raised to 360°, 19.03 per cent. of

a dark reddish-brown oil distilled, which had a penetrating empyreumatic odour; it had a sp. gr. 0.920 at 15° and iodine number 98.10—102.68. The last fraction, obtained at temperatures above 360°, was equal to 12.93 per cent. of the total weight of the copal, and formed a greenish-brown, viscous oil, which had an odour similar to that of turpentine; it had a sp. gr. 0.9805 at 15°, and iodine number 42.68. The residue, which amounted to 13.87 per cent., consisted of tar and carbon. The Java fossil copal does not appear to be related to any of the known kinds of copal.

E. W. W.

Japan Lacquer (Ki-Urushi). ALEXANDER TSCHIRCH and A. B. STEVENS (*Arch. Pharm.*, 1905, 243, 504—553).—The paper contains an account of work done previously on the subject, a description of the specific action of the poison (producing local dermatitis) contained in the lacquer, this poison being shown not to be volatile, as hitherto supposed, but to consist of an oily substance soluble in light petroleum, and a summary of numerous oxydases, in which connection it is shown that enzymes of this character are associated with many “gums” (“*Gummis*”), and the name of *gummas* is proposed for such enzymes.

Owing to the difficulties attending the investigation, the results were somewhat meagre. Of the sample examined, 72 per cent. dissolved in alcohol; water then dissolved 4.0 per cent., leaving 2.3 per cent. of residue; the remaining 21 per cent. must have been water. The portion soluble in alcohol, called by Yoshida (*Trans.*, 1883, 43, 472) urushic acid or lacquer acid, and by Bertrand laccol, has not the character of an acid, and in consequence the name of *urushin* is proposed for it. Under the influence of various reagents, including acids, alkali hydroxides, and the enzyme contained in the lacquer when moist air is present, urushin is transformed into an exceedingly stable substance, *oxyurushin* (Yoshida's oxyurushic acid), to which fact the value of the lacquer is due. It is noteworthy that both urushin and oxyurushin contain nitrogen, for they are the first substances belonging to the class of resins in which nitrogen has been detected. Urushin contains C 71.0—73.6, H 7.8—10.5, N 0.2—1.8, ash 0.2—1.2; oxyurushin: C 70.9—71.8, H 8.1—8.3, N 0.1—1.6, ash 0.0—0.8 per cent.

Urushin can be separated into two fractions respectively soluble (78 per cent.) and insoluble in light petroleum. The soluble fraction can be separated further into a non-volatile *poison* and a mixture of *gum* and *enzyme* (lacquer-gum-mase, Bertrand's laccase, *Abstr.*, 1895, i, 385, 386) which could not be separated into its constituents. This mixture contained C 41.7, H 6.0, N 0.61, ash 5.2 per cent.; it yields pyrrole, not ammonia, when heated with solid potassium hydroxide; mucic acid, calcium oxalate, and tartaric acid when oxidised with nitric acid; and *r* and *r*+*l*-sorbinazone when hydrolysed with dilute sulphuric acid and treated with phenylhydrazine. The lacquer also contains acetic acid.

C. F. B.

Prulaurasin, a Crystalline Cyanogenetic Glucoside obtained from the Leaves of Cherry Laurel. HENRI HÉRISSEY (*Compt. rend.*, 1905, 141, 959—961).—Previous attempts to extract

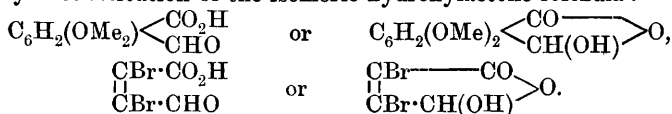
the cyanogenetic principle from the leaves of the cherry-laurel in a pure state have not been successful (compare Lehmann, *Neues Rep. Pharm.*, 1874, 23, 449; Jouck, *Abstr.*, 1905, i, 912), and in the present paper details are given of a method whereby the crystalline glucoside prulaurasin can be obtained from the fresh leaves of the plant. *Prulaurasin*, $C_{14}H_{17}O_6N$, crystallises from a mixture of ethyl acetate and toluene or chloroform in long, slender, colourless, flexible needles melting at $120-122^\circ$, has $\alpha_D - 52.75^\circ$, and a slightly bitter taste, is readily soluble in water, alcohol, or ethyl acetate, slightly soluble in ether. It is hydrolysed by emulsin, yielding hydrogen cyanide, dextrose, and benzaldehyde, and is therefore an isomeride of Fischer's benzalnitride-glucoside (*Abstr.*, 1895, i, 553) and of Bourquelot and Danjou's sambunigrin (*Abstr.*, 1905, i, 912).

M. A. W.

The Saponin of the White Soapwort. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1905, 243, 496—504).—Gypsophila-saponin, obtained from the root of the Levantine soapwort, appears to be a mixture of two homologues, $C_{18}H_{28}O_{10}$ and $C_{19}H_{30}O_{10}$. When it is hydrolysed, sapogenin, an arabinose, and another sugar are formed in about equal quantities.

C. F. B.

Action of Grignard's Reagent on α - or γ -Aldehydo-acids. HUGO SIMONIS, E. MARBEN, and E. MERMOD (*Ber.*, 1905, 38, 3981—3985. Compare Liebermann, *Abstr.*, 1886, 550; Bistrzycki, *ibid.*, 1888, 1210; 1890, 969; 1891, 746).—The reaction between α - and γ -aldehydo-acids and Grignard's reagent has been studied in order to settle the question as to whether the compounds have the aldehydo-constitution or the isomeric hydroxylactone formula:



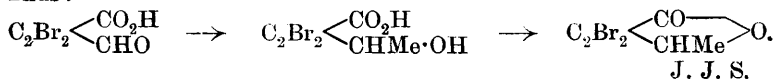
α -Methylphthalide (Giebe, *Abstr.*, 1897, i, 62) is obtained by the action of an excess of methyl magnesium iodide on phthalaldehydic acid and α -methylmeconine (m. p. 101°) by the action of the same reagent on opianic acid.

3 : 4-Dibromo-2-methyldihydrofuranone, $\begin{array}{c} CBr \text{---} CO \\ | \\ CBr \cdot CHMe \end{array} > O$, obtained

from magnesium methyl iodide and mucobromic acid, crystallises from water in flat needles melting at 69.5° . The corresponding *ethyl* derivative crystallises from light petroleum and melts at 51.5° .

3 : 4-Dichloro-2-methyldihydrofuranone distils at 120° under 12 mm. pressure and the corresponding *ethyl* compound at $109-110^\circ$ under 11 mm. pressure.

These reactions indicate the aldehydic structure of all the acids
Thus:



J. J. S.

Arylamine Derivatives of Furfuraldehyde and their Conversion into Pyridine Compounds. THEODOR ZINCKE and G. MÜHLHAUSEN (*Ber.*, 1905, 38, 3824—3829).—The dianilide, $C_{17}H_{16}ON_2$, probably $C_4OH_3 \cdot CH(C_6H_4 \cdot NH_2)_2 \cdot H_2O$, prepared by the action of aniline and its hydrochloride on furfuraldehyde (Stenhouse, *Annalen*, 1870, 156, 199), yields a *hydrobromide* which crystallises from hot alcohol in long, violet-red needles and melts and decomposes at 165—166°. The *di-p-toluidide* yields a *hydrochloride*, $C_{19}H_{20}ON_2 \cdot HCl$, which crystallises from alcohol in long, slender, violet-red needles and melts and decomposes at 173—178°.

3-Hydroxy-1-phenylpyridinium chloride, $OH \cdot C_5NH_4PhCl$, prepared by boiling the hydrobromide of the dianilide with alcohol or acetic acid, crystallises from absolute alcohol in stout, colourless needles or spangles, or in compact, rhombic crystals, and melts at 210—212°; the *platinichloride* crystallises from hot water in long, orange-yellow needles and melts and decomposes at 204—206° after losing its water of crystallisation at 100°; the *bromide*, $C_{11}H_{10}ONBr$, forms colourless needles and melts at 175°.

3-Hydroxy-1-p-tolylpyridinium chloride, $OH \cdot C_5NH_4Cl \cdot C_6H_4Me$, crystallises from hot water in long, broad spangles or in small needles, melts at 210—212°, and is more soluble than the phenyl compound; the *platinichloride* crystallises from hot water in orange-yellow, hydrated needles and melts and decomposes at 216°.

T. M. L.

2-Methyl-6-pyrophthalone. A. SCHOLZE (*Ber.*, 1905, 38, 4022).—The formula of the sodium salt of 2-methyl-6-pyrophthalone should be $C_6H_4 \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ C(ONa) \end{smallmatrix} \rangle C \cdot C_5NH_3Me$ instead of that given formerly (*Abstr.*, 1905, i, 825).

W. A. D.

Influence of Light and Heat on the Chlorination and Bromination of Homologues of Thiophen. II. ST. OPOLSKI (*Bull. Acad. Sci. Cracow*, 1905, 548—557. Compare *Abstr.*, 1905, i, 367).—The substitution of halogen in the ring of 2-alkylthiophens takes place in position 5. The bromination product of 2-methylthiophen is 5-bromo-2-methylthiophen, as when treated with methyl iodide and sodium at the laboratory temperature it is converted slowly into 2:5-dimethylthiophen. Bromination of 2-ethylthiophen at high temperatures leads to the formation of 5-bromo-2-ethylthiophen, which is formed also under the influence of light (*loc. cit.*).

Chlorination of 2-ethylthiophen at its boiling point or under the influence of light leads to the formation of 5-chloro-2-ethylthiophen, which is a liquid of mild odour, boils at 85—88° under 37 mm. or at 175.5° (corr.) under 737 mm. pressure, does not solidify at -75°, and becomes yellow on exposure to light. It has the sp. gr. 1.1629 at 12.3°/4° and n_D 1.5330 at 12.3°, and gives the indophenin and Laubenheimer's colour reactions only indistinctly and with difficulty.

On chlorination under the influence of heat or light, 2-butylthiophen yields chiefly 5-chloro-2-butylthiophen, which is a colourless liquid of mild odour, becomes yellow on exposure to light, boils at 117—118° (corr.) under 38 mm. pressure, and has the sp. gr. 1.0842

at $17^{\circ}/4^{\circ}$ and n_D 1.5162. 5-Bromo-2-butylthiophen, formed by bromination of 2-butylthiophen in the same manner, is a colourless liquid of mild odour, boils at 138.5° (corr.) under 42 mm. pressure, and has the sp. gr. 1.3369 at $20.5^{\circ}/4^{\circ}$, and n_D 1.5398. 5-Chloro- and 5-bromo-2-butylthiophen give the colour reactions with isatin and phenanthraquinone only indistinctly and with difficulty.

3-Methylthiophen has the sp. gr. 1.0247 at $15.8^{\circ}/4^{\circ}$ and n_D 1.5218. When boiled with alcoholic ammonia, the product obtained on chlorination at the boiling point or under the influence of light yields only a small amount of a substance which forms a solid *hydrochloride* and a yellow, amorphous *platinichloride*. The chief product of the chlorination is *chloro-3-methylthiophen*, which is obtained as a colourless liquid boiling at 154° (corr.) under 733 mm. pressure; it has the sp. gr. 1.2197 at $19.6^{\circ}/4^{\circ}$, and n_D 1.5394, and gives a green coloration with isatin in sulphuric acid solution and a glistening emerald-green coloration with phenanthraquinone and sulphuric acid in glacial acetic acid solution.

Bromination of 3-methylthiophen under the same conditions leads to the formation of bromo-3-methylthiophen, together with a considerable amount of a product substituted in the side-chain. This, when boiled with alcoholic ammonia, yields *trithienylamine*, $N(CH_2 \cdot C_4H_3S)_3$, which forms a white, crystalline *hydrobromide* and *hydrochloride* melting at 124.5 — 127° ; these give yellow to red, amorphous *platinichlorides*. Bromo-3-methylthiophen is a colourless liquid, which becomes yellow on exposure to light, boils at 175° (corr.) under 729 mm., and has the sp. gr. 1.5844 at $17.5^{\circ}/4^{\circ}$, and n_D 1.5731. It gives Laubheimer's green coloration and a green coloration changing to blue with isatin.

The distillation residues obtained in the preparation of homologues of thiophen by Fittig's reaction are explosive, evolve hydrogen and acetylene when treated with water, and contain therefore probably sodium carbide together with unchanged sodium. G. Y.

Angostura Bases. HEINRICH BECKURTS and GUSTAV FRERICHS [and, in part, A. LACHWITZ] (*Arch. Pharm.*, 1905, 243, 470—493. Compare Körner and Boehringer, *Abstr.*, 1884, 341; Beckurts and others, *Abstr.*, 1892, 642; 1896, i, 66; 1904, i, 84).—The *nitrate* with $1\frac{1}{2}H_2O$, *dichromate*, and *acetate* of the monoacid base cusparine, $C_{20}H_{19}O_3N$, are described for the first time; the last loses its acetic acid when kept in a desiccator over sulphuric acid.

When a solution of cusparine in dilute hydrochloric acid is mixed with a limited amount of bromine dissolved in water and ammonia is added until the reaction is alkaline, crystalline *monobromocusparine*, $C_{20}H_{18}O_3NBr$, melting at 91° , is precipitated; the crystalline *hydrochloride*, *platinichloride*, and *aurichloride* were prepared and analysed; the last two melt at 210 — 212° and 188 — 190° respectively. When excess of bromine is added to a solution of cusparine in dilute hydrobromic acid, amorphous, yellow *bromocusparine tetrabromide*, melting at 163 — 164° , is precipitated; when this is treated with alcohol, it yields the yellow, amorphous *tribromide* melting at 163 — 165° ; when heated at 105° , the *dibromide*, which melts at 163 — 166° ; from a warm solution

of any of these in alcohol, *bromocusparine hydrobromide*, melting at 239—241°, crystallises. Boiling with dilute potassium hydroxide solution, or reduction with either zinc and sulphuric acid or hydrogen sulphide, converts the tetrabromide into monobromocusparine itself.

With cusparine in chloroform solution, bromine yields a precipitate of monobromocusparinedibromide, whilst bromocusparine hydrobromide remains in solution. In acetic acid solution, bromine converts cusparine into monobromocusparine triibromide, together with some tetrabromide and bromocusparine hydrobromide.

When a solution of sodium hypochlorite is added to a solution of cusparine in acetic acid, yellow, amorphous *dichlorocusparine*, $C_{20}H_{17}O_3NCl_2 \cdot 2H_2O$, is precipitated.

When excess of iodine solution is added to a solution of cusparine hydrochloride, the dark-coloured *hydriodide* of *cusparine di-iodide*, $C_{20}H_{19}O_3N \cdot HI \cdot I_2 \cdot 2H_2O$, is precipitated; this crystallises unchanged from alcohol.

Ethylcusparine, $C_{22}H_{23}O_3N$, crystallises with 1 molecule of alcohol; the compound melts at 116°. The *hydrochloride* and *platinichloride* of this mono-acid base were analysed; the latter melts and decomposes at 186°.

Cusparine does not react with benzoyl chloride.

Of galipidine, $C_{19}H_{19}O_3N$, a monoacid base, the *hydriodide*, *sulphate*, and *hydrogen sulphate* were analysed. The base itself yields proto-catechuic acid when heated with fused potassium hydroxide. From a solution of galipidine hydrobromide, excess of bromine precipitates the *pentabromide*, $C_{19}H_{19}O_3N \cdot HBr \cdot Br_5$; when heated at 105°, this leaves the dibromide, $C_{19}H_{19}O_3N \cdot HBr \cdot Br_2$, whilst when washed with cold alcohol, $C_{19}H_{19}O_3N \cdot HBr \cdot Br$ is obtained.

Galipidine methochloride, $C_{19}H_{19}O_3N \cdot MeCl$, which crystallises in greenish-yellow needles, and the corresponding *platinichloride* and *aurichloride*, which melt at 187° and 119° respectively, were analysed. When the methiodide is warmed with dilute aqueous potassium hydroxide, the monoacid base, *methylgalipidine*, $C_{20}H_{21}O_3N$, is formed; this crystallises in needles and melts at 166°; its yellow *hydrochloride* and *platinichloride*, the latter melting and decomposing at 200°, were analysed.

When galipidine is heated with ethyl iodide for twelve hours at 100°, the *ethiodide*, $C_{19}H_{19}O_3N \cdot EtI$, is formed; this crystallises with $1H_2O$ and melts at 102° to a milky liquid which becomes clear at 140—142°; the corresponding *aurichloride*, which is amorphous and melts at about 142°, was analysed.

Galipidine does not form additive compounds with methylene iodide, or with ethylene iodide or bromide.

C. F. B.

Crystalline Alkaloid of Calycanthus Glauca. II. HARRY M. GORDIN (*J. Amer. Chem. Soc.*, 1905, 27, 1418—1429. Compare Abstr., 1905, i, 295).—A detailed description is given of calycanthine *nitrate*, *sulphates*, *aurichloride*, *picrate*, *oxalates*, *mercurichloride*, and *tartrates*. Calycanthine *nitrosoamine*, $C_{11}H_{13}N_2 \cdot NO$, becomes brown at 172° and melts and decomposes at 175—176°. The alkaloid contains one methyl group attached to nitrogen. Attempts to prepare acetyl and

benzoyl derivatives were unsuccessful. Methyl iodide converts calycanthine into a mixture of several substances which are at present under investigation. By the action of sulphuric acid on the alkaloid, a *sulphonic acid* is produced ; its *barium* salt was prepared.

E. G.

[The Alkaloids of] *Bocconia Cordata*. JULIUS O. SCHLOTTERBECK and WALTER H. BLOME (*Pharm. Rev.*, 1905, 23, 310—321. Compare Murrill and Schlotterbeck, Abstr., 1900, i, 686).—When β -homochelidonine is heated in a sealed tube with strong hydrochloric acid, methyl chloride is produced together with a mixture of substances which were not isolated. An attempt was made to effect the oxidation of the alkaloid with alcoholic solution of iodine, but without success. Phosphorus pentachloride reacts with β -homochelidonine with formation of a yellow, crystalline *substance* which melts and decomposes at about 198° and is apparently the hydrochloride of an alkaloid not containing substituted chlorine in its molecule. An acetyl derivative of β -homochelidonine could not be obtained. On fusing the alkaloid with potassium hydroxide, protocathechuic acid is produced.

E. G.

Formation of Incompletely Hydrogenated Pyridines by the Wyschnegradsky-Ladenburg Reaction. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1905, 38, 3834).—A question of priority (compare Königs and Bernhart, Abstr., 1905, i, 824 ; Tschitschibabin, Abstr., 1902, i, 825).

A Tetrahydroaldehydecollidine. [2-Methyl-5-ethyltetrahydropyridine.] WILHELM KÖNIGS and KARL BERNHART (*Ber.*, 1905, 38, 3928—3933. Compare Abstr., 1905, i, 824 ; Dürkopf, Abstr., 1888, 817 ; Levy and Wolfenstein, Abstr., 1895, i, 683 ; 1896, i, 624 ; Marcuse and Wolfenstein, Abstr., 1901, i, 608).—Reduction of 2-methyl-5-ethylpyridine with sodium and boiling absolute alcohol leads to the formation of the tetrahydro- and hexahydro-bases ; these are separated by conversion into the hydrobromides and treatment with cold acetone, in which 2-methyl-5-ethylpiperidine hydrobromide is insoluble. This crystallises from hot acetone in colourless needles and melts at 175° . 2-Methyl-5-ethyltetrahydropyridine hydrobromide, which is soluble in cold acetone, is converted into 2-methyl-5-ethyltetrahydropyridine dibromide hydrobromide, $C_8H_{15}NBr_2 \cdot HBr$, by means of bromine in chloroform solution, which, after removal of copellidine and isocopellidine hydrobromides by extraction with cold ethyl acetate, crystallises from a mixture of chloroform and ethyl acetate in colourless needles and melts and decomposes at 187° .

2-Methyl-5-ethyltetrahydropyridine dibromide, $C_8H_{15}NBr_2$, is obtained on treatment of its hydrobromide with aqueous sodium carbonate, as an oil which has an odour faintly resembling that of camphor, volatilises on exposure to the air, is moderately stable towards permanganate in cold dilute sulphuric or nitric acid solution, and with sodium nitrite in sulphuric acid solution forms the *nitroso*-derivative. This separates from light petroleum in colourless crystals, melts at 106 — 107° , gives a green coloration with Liebermann's

nitrosoamine reaction, and when boiled with concentrated hydrobromic acid loses the nitroso-group and forms the hydrobromide.

2-Methyl-5-ethyltetrahydropyridine, $C_8H_{15}N$, is obtained in the form of its hydrobromide, $C_8H_{15}N \cdot HBr$, by reducing the dibromide hydrobromide with zinc dust and dilute sulphuric acid at the laboratory temperature and treating the product with hydrobromic acid. The hydrobromide forms a colourless, crystalline mass, melts at $86-93^\circ$, or, after heating at 100° , at $98-99^\circ$, and with bromine in chloroform solution forms the dibromide hydrobromide. The base is a mobile, colourless oil, which has a pyridine-like odour and distils at $167-168^\circ$ under 720 mm. pressure. The oxalate forms a colourless, crystalline powder and melts at $153-155^\circ$; the ditartrate is easily soluble in water or alcohol; the picrate forms yellow plates melting at $138-141^\circ$; the crystalline aurichloride melts at 83° ; the yellow, crystalline platinichloride melts and decomposes at 190° . In dilute sulphuric acid solution, the base decolorises potassium permanganate at 0° ; with carbon disulphide in ethereal solution, it forms the crystalline thiocarbamate, which melts at $73-74^\circ$. The base interacts with phenylthiocarbamide with development of heat and formation of an oil which solidifies to a crystalline mass melting at 80° . G. Y.

Compounds of Quinquevalent Chromium. RUDOLF F. WEINLAND and WALTER FRIDRICH (*Ber.*, 1905, **38**, 3784—3787).—Pyridinium tetrachlorohydroxychromanate, $C_5NH_5 \cdot CrCl_4 \cdot OH \cdot H_2O$, formed by the successive action of concentrated hydrochloric acid and pyridine on chromic acid at $10-12^\circ$, crystallises in glistening, reddish-brown leaflets or microscopic, orange-yellow, hexagonal plates.

Quinolinium tetrachlorohydroxychromanate, $C_9NH_7 \cdot CrCl_4 \cdot OH \cdot 2H_2O$, prepared in similar manner, crystallises in glistening, reddish-brown needles or microscopic, long, orange-yellow plates, and decomposes on exposure to air, becoming orange-red with loss of chlorine. G. Y.

Condensation of 2:4:6-Trimethylpyridine with Benzaldehyde. WILHELM KÖNIGS and ALFONS VON BENTHEIM (*Ber.*, 1905, **38**, 3907—3911. Compare Königs and Mengel, *Abstr.*, 1904, i, 527).—When heated with 1 mol. of benzaldehyde and zinc chloride in a sealed tube at $170-180^\circ$, 2:4:6-trimethylpyridine yields the monobenzylidene derivative (2:4-dimethyl- α -stilbazole, Dubke, *Abstr.*, 1894, i, 207) without intermixture of the alkine; the platinichloride melts at 245° (m. p. $230-232^\circ$, Dubke). Oxidation of the dimethylstilbazole with nitric acid leads to the formation of 2:4-dimethylpyridine-6-carboxylic acid (Altar, *Abstr.*, 1887, 378).

When heated with 3 mols. of benzaldehyde and zinc chloride in a sealed tube at $170-180^\circ$, 2:4:6-trimethylpyridine forms the tribenzylidene derivative [2:4:6-tristyrylpyridine], $C_5NH_2(CH:CHPh)_3$, which crystallises in glistening, colourless needles, melts at $187-188^\circ$, dissolves readily in benzene, chloroform, or carbon disulphide, forming blue, fluorescent solutions which become yellow on addition of a trace of acid. The acetate crystallises from glacial acetic acid as a yellow salt with blue fluorescence which easily loses acetic acid; the picrate,

$C_{29}H_{23}N, C_6H_5O_7N, \frac{1}{2}C_8H_6O$, crystallises in golden needles and melts at $235-236^\circ$; the *platinichloride* forms a yellow powder. When oxidised with nitric acid, tristyrylpyridine yields pyridine-2:4:6-tricarboxylic acid (Voigt, Abstr., 1885, 812). G. Y.

Condensations of 2-Methyl-5-ethylpyridine and of 2:4-Lutidine with Aldehydes. G. LANGER (*Ber.*, 1905, 38, 3704—3709. Compare Abstr., 1888, 65, 608; 1890, 1437).—4'-Methyl-5-ethyl-2-stilbazole, $C_{16}H_{17}N$, obtained by heating 2-methyl-5-ethylpyridine and *p*-tolualdehyde with zinc chloride at 210° for sixteen hours, crystallises from alcohol in colourless needles melting at 94° , and readily soluble in alcohol, ether, chloroform, or glacial acetic acid. The *hydrochloride*, $C_{16}H_{17}N, HCl$, is precipitated from its alcoholic solution by ether as small, yellow needles. The *mercurichloride* melts at 227° , the *picrate* at $201-202^\circ$, the *methiodide* at 212° , and the *ethiodide* at 233° . The corresponding *stilbazoline*, $C_{16}H_{25}N$, distils at $202-203^\circ$ under 14 mm. pressure. Its salts form pasty masses. 4'-Methyl-5-ethyl-2-stilbazole, $C_{16}H_{19}N$, obtained by reducing the stilbazole with hydriodic acid at 160° , distils at 198° under 18 mm. pressure. The *hydrochloride* crystallises in yellow needles and melts at 42° ; the *platinichloride* forms reddish-yellow needles and melts at $156-157^\circ$.

4:4'-Dimethylstilbazole, $C_{15}H_{15}N$, obtained by the condensation of 2:4-lutidine with *p*-tolualdehyde in the presence of zinc chloride at $180-190^\circ$, is only sparingly soluble in alcohol, acetone, or benzene and melts at 202° . The *mercurichloride* melts at 160° , the *aurichloride* at 170° , the *platinichloride* at 208° , and the *hydrobromide* at 115° . Its *dihydro*-derivative, $C_{15}H_{17}N$, crystallises from alcohol in glistening, white plates and melts at 103° . The *platinichloride* melts at 168° and the *aurichloride* at 142° .

4:4'-Dimethylstilbazoline, $C_{15}H_{23}N$, is an oil; its *platinichloride* melts at $104-105^\circ$.

4-Methylpicolyl-*p*-tolylalkine [β -hydroxy-4:4'-dimethyldihydrostilbazole], $C_{15}H_{17}ON$, is obtained as a by-product in the preparation of 4:4'-dimethylstilbazole. It dissolves readily in alcohol and melts at 64° . The *mercurichloride* melts at 197° and the *platinichloride* at 181° .

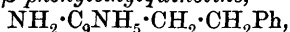
Phthalic anhydride and 2:4-lutidine yield a *phthalone*, $C_{15}H_{11}O_2N$, melting at 262° . Formaldehyde and 2:4-lutidine yield 2:4-lutidylalkine. J. J. S.

Carbostyryl as a By-product in a Molasses Furnace. EDMUND O. VON LIPPMANN (*Ber.*, 1905, 38, 3829—3830).—Three hundred grams of a crystalline sublimate were obtained from a crack in the masonry of a furnace used for the ignition of sugar-liquors. A part of this was soluble in water, but the most important constituent was separated by extracting with alcohol and ether, and after crystallisation from alcohol was found to be carbostyryl, $C_6H_4 \begin{matrix} \text{CH:CH} \\ \text{N} = \text{C:OH} \end{matrix}$ T. M. L.

Condensation of Anthranilic Acid with Ethyl Benzoylacetate. STEFAN VON NIEMENTOWSKI (*Bull. Acad. Sci. Cracow*, 1905, 285—286).—The condensation of anthranilic acid with ethyl benzoyl-

acetate leads to the formation of various products, depending on the proportions of the interacting substances, the purity of the materials, and the duration and the temperature of the reaction. The chief product is ethyl 4-hydroxy-2-phenylquinoline-3-carboxylate, melting at 262° ; at high temperatures, up to 240° , or on prolonged heating, triphenylbenzene is formed. A *substance*, $C_{32}H_{20}O_5N_2$, which resembles the sparingly soluble condensation products of ethyl acetoacetate with anthranilic and *m*-bromoanthranilic acids, benzanilide, a *substance* which resembles and melts a few degrees higher than ethyl 4-hydroxy-2-phenylquinoline-3-carboxylate, and a *derivative* melting at 318° are formed also. G. Y.

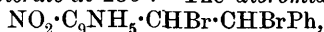
Reaction between Nitroquinaldines and Aldehydes. ALBERT SCHMIDT (*Ber.*, 1905, 38, 3715—3723).—8-Nitro-2-styrylquinoline, $NO_2 \cdot C_9NH_5 \cdot CH:CHPh$, is obtained when 8-nitroquinaldine and benzaldehyde are heated in an oil-bath at 150° for 4—5 hours. It crystallises from alcohol in pale yellow needles, melts at 142° , and dissolves readily in most organic solvents. The *hydrochloride* crystallises in reddish-yellow, glistening plates, which decompose at about 140° and are completely molten at 172° . The *platinichloride* darkens at 231° and is not melted at 290° ; the *aurichloride* forms small, orange needles melting at 233° , and the *mercurichloride* similar needles melting at 224° . When reduced with tin and hydrochloric acid, the base yields 8-amino-2- β -phenylethylquinoline,



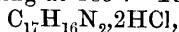
which crystallises from dilute alcohol in yellow needles melting at 122° . The *hydrochloride*, $C_{17}H_{16}N_2 \cdot 2HCl$, crystallises from alcohol in carmine-red needles, begins to decompose at 199° , melts at 211° , and is decomposed by water. The *platinichloride* decomposes at 220° .

8-Nitro-2-p-methylstyrylquinoline, $NO_2 \cdot C_9NH_5 \cdot CH:CH \cdot C_6H_4Me$, crystallises in pale yellow needles and melts at 145° . The *hydrochloride*, $C_{18}H_{14}O_2N_2 \cdot HCl \cdot H_2O$, crystallises in purplish-red plates, is decomposed by water, and melts and decomposes at 179 — 180° . The *platinichloride* forms golden-yellow needles which begin to decompose at 243° . The *aurichloride* melts at 221° and the *mercurichloride* at 226° . When reduced, the base yields 8-amino-2-p-tolyethylquinoline, $NH_2 \cdot C_9NH_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_4Me$, which crystallises in yellow needles melting at 161° . The *hydrochloride*, $C_{18}H_{18}N_2 \cdot 2HCl$, crystallises in carmine-red needles and melts at about 222° ; the *platinichloride*, $(C_{18}H_{18}N_2)_2 \cdot H_2PtCl_6$, decomposes at 230° .

5-Nitro-2-styrylquinoline crystallises from dilute alcohol in very long, pale yellow needles melting at 127° . The *hydrochloride* forms golden-yellow needles, which sinter at 204° and melt at 213° . The *platinichloride* begins to decompose at 199° ; the *aurichloride* sinters at 218° and melts at 237° ; the *mercurichloride* melts indefinitely at about 249 — 250° and the *picrate* at 236° . The *dibromide*,



crystallises in colourless needles and melts and decomposes at 164° . When reduced, the base yields 5-amino-2- β -phenylethylquinoline in the form of yellow needles melting at 185° . The *hydrochloride*,

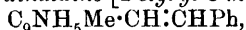


crystallises in pale red needles, begins to decompose at 229° , and melts at 251° . The *platinichloride* forms minute, golden-brown needles and decomposes at 262° .

5-Nitro-2-p-methylstyrylquinoline melts at 135° , its *hydrochloride* sinters at 216° and melts at 225° , the *platinichloride* decomposes at 220° , the *mercurichloride* sinters at 244° and melts at 256° , and the *picrate* melts and decomposes at 255° . The *dibromide*, $C_{18}H_{14}O_2N_2Br_2$, crystallises in snow-white needles, becomes yellow at 120° , and then decomposes. When reduced, the base yields 5-amino-2-p-tolyethylquinoline, $C_{18}H_{18}N_2$, which forms yellow needles melting at 173° ; the *hydrochloride* melts at 243° .

6-Nitro-2-styrylquinoline forms pale yellow needles, melts at 192° , and is insoluble in water or ether. The *hydrochloride* crystallises in long, pale yellow needles and melts at 205° , the *platinichloride* begins to decompose at 200° , the *aurichloride* melts at 218° , and the *mercurichloride* at about 245° after sintering at 239° . When reduced, the base yields 6-amino-2- β -phenylethylquinoline, which melts at 204° . The *hydrochloride* becomes red at 140° and melts at 253° . The *platinichloride* is not molten at 290° , and the *mercurichloride* begins to decompose at 150° .
J. J. S.

Condensation of o-Methylquinaldine [2:8-Dimethylquinoline] with Aldehydes. MARTIN HOFFMANN (*Ber.*, 1905, 38, 3709—3714). —Benzylidene-o-methylquinaldine [2-styryl-8-methylquinoline],



obtained by the action of benzaldehyde on 2:8-dimethylquinoline (Doebner and von Miller, *Abstr.*, 1884, 184) at 150 — 155° , crystallises from alcohol in colourless, transparent, hexagonal plates, melting at 72° and soluble in all organic solvents. The *hydrochloride* crystallises in large, yellow needles and melts at 113° . The *mercurichloride* forms golden-yellow, glistening plates melting at 244° ; the *platinichloride* melts at 229 — 230° , the *aurichloride* at 214° , and the *picrate* crystallises from methyl alcohol in small, yellow needles.

2-o-Nitrostyryl-8-methylquinoline, $C_{18}H_{14}O_2N_2$, crystallises in felted needles melting at 96° . The *hydrochloride* forms yellow needles, the *mercurichloride* also yellow needles melting above 280° ; the *platinichloride* melts at 247° , and the *aurichloride* at 238° .

2-m-Nitrostyryl-8-methylquinoline forms a pale yellow powder melting at 109° . The *hydrochloride* melts at 223° , the *mercurichloride* at 249 — 250° , the *platinichloride* at 269° , and the *aurichloride* melts and decomposes at 209° .

2-p-Nitrostyryl-8-methylquinoline forms dark red crystals melting at 112° . The *hydrochloride* melts at 125 — 126° , the *aurichloride* at 239° , and the *platinichloride* at 264° .

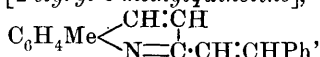
2-Methylenedioxy-2-styryl-8-methylquinoline, $C_{19}H_{15}O_2N$, obtained from piperonal and 2:8-dimethylquinoline at 120° , crystallises in colourless, glistening plates and melts at 176° . The *hydrochloride* forms yellow needles melting at 244° , and the *picrate* copper-coloured, glistening plates melting at 239 — 240° . The *mercurichloride*, *aurichloride*, and *platinichloride* are oils.

Formaldehyde and 2 : 8-dimethylquinoline yield a product with no definite boiling point, but from this a *benzoyl* derivative, $C_{19}H_{17}O_2N$, melting at 118° , has been prepared.

The following salts of 8-methyl-2- Δ^8 -butenylquinoline have been prepared: *hydrochloride*, yellow crystals melting at $198-199^\circ$, *mercurichloride*, colourless needles melting at $212-213^\circ$, *aurichloride*, golden-yellow needles melting at 208° . From 8-methyl-2-isobutenylquinoline, the *hydrochloride* melting at 254° , *aurichloride* at $190-191^\circ$, and *picrate* at $164-165^\circ$ have been obtained. J. J. S.

Condensation of *p*-Methylquinaldine [2:6-Dimethylquinoline] with Aromatic Aldehydes. GEORG GASDA (*Ber.*, 1905, 38, 3699—3704).—2 : 6-Dimethylquinoline (Doebner and von Miller, *Abstr.*, 1884, 184) readily condenses with aromatic aldehydes, especially in the presence of zinc chloride, yielding derivatives of 2-irazole [2-styrylquinoline], $C_6H_4 \begin{smallmatrix} \text{CH:CH} \\ | \\ \text{N}=\text{C}\cdot\text{CH:CHPh} \end{smallmatrix}$, so called on account of the optical properties of the bases thus formed.

6-Methyl-2-irazole [2-styryl-6-methylquinoline],



obtained from 2 : 6-dimethylquinoline and benzaldehyde, crystallises from alcohol in large, colourless, strongly refractive prisms melting at 137° and readily soluble in chloroform or acetone. The *hydrochloride* crystallises in microscopic, greenish-yellow needles, becomes brown at 215° , and melts at 243° . The *aurichloride* crystallises from alcohol in golden-yellow needles and melts at 215° ; the *platinichloride* decomposes at 279° , the *mercurichloride* melts at 223° , and the *picrate* at 234° . All the salts are practically insoluble in water or ether. The *dibromide*, $C_{18}H_{15}NBr_2$, crystallises from alcohol in colourless plates melting at 169° .

When reduced with sodium and alcohol, the base yields a hexahydro-derivative. 6-Methyl-2-irazoline, $C_{18}H_{21}N$, which crystallises in colourless needles melting at 66° , distils at 254° under 25 mm. pressure and dissolves in most organic solvents. The *hydrochloride* is hygroscopic, crystallises in small, colourless needles, sinters at 202° , and melts at $209-210^\circ$. The *benzoyl* derivative melts at 102° .

2-m-Nitrostyryl-6-methylquinoline, $C_9H_9Me\cdot CH:CH\cdot C_6H_4\cdot NO_2$, obtained from 6-methylquinaldine and *m*-nitrobenzaldehyde, crystallises from alcohol in short, yellow prisms melting at 201° , and is not readily soluble in the ordinary organic solvents. The *hydrochloride* becomes brown at 257° , the *platinichloride* crystallises in orange-coloured needles and is not decomposed at 300° , the *mercurichloride* melts at 254° and dissolves in hydrochloric acid and alcohol, the *picrate* melts at 271° , and the *dibromide* becomes brown at 205° and melts at 209° .

2-p-Hydroxystyryl-6-methylquinoline crystallises in glistening needles, melts at 249° , and is only sparingly soluble in water or ether. The *hydrochloride* crystallises in brick-red needles, dissolves in water, alcohol, or hydrochloric acid, and is not decomposed at 300° . The

platinichloride becomes brown at 249°, the *mercurichloride* melts at 262°, the *picrate* at 251°, and the *dibromide* at 265—266°, after darkening at 255°.

The corresponding *hexahydro*-derivative, $C_{18}H_{21}ON$, crystallises from alcohol in glistening needles, melts at 101—102°, and dissolves readily in most organic solvents. The *hydrochloride* forms pale yellow needles and melts at 257°; the *picrate* melts at 271° and is readily soluble in water or alcohol.

2-p-Methylstyryl-6-methylquinoline forms large, colourless, strongly refractive needles and melts at 144°; the *hydrochloride* forms yellow needles, sinters at 230°, and melts at 251°; the *aurichloride* crystallises in golden-red needles, melts at 227°, and is sparingly soluble in alcohol. The *platinichloride* melts at 282°, the *mercurichloride* at 209—210°, and the *dibromide* at 167°.

The corresponding *hexahydro*-derivative melts at 68°, its *hydrochloride* at 232°, its *platinichloride* at 224°, and its *benzoyl* derivative at 75°.

J. J. S.

Constitution of Cyanine Dyes. GILBERT BOOK (*Ber.*, 1905, 38, 3804—3806).—The colour of ethyl-red is retained by its di-iodide, because, although the unsaturated linking between the two quinoline groups disappears, one of them retains a quinonoid structure.

When 2:4-dimethylquinolinium methiodide is acted on by alcoholic potash, no change in colour is observed when the solution is kept in a corked flask or in a current of hydrogen; the appearance of the colour and the formation of the dye are due to atmospheric oxidation, and the process is thus entirely distinct from that which gives rise to the cyanine dyes.

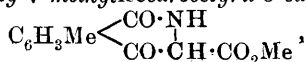
T. M. L.

isoQuinoline Derivatives from 4-Methylphthalic Acid. WALDEMAR FINDEKLEE (*Ber.*, 1905, 38, 3542—3553).—The acid was prepared from *m*-toluidine, which was converted into *m*-toluonitrile, nitrated in the para-position, reduced, diazotised, and converted into dicyanotoluene, which was hydrolysed to 4-methylphthalic acid. Particulars are given of the methods adopted and the properties of the intermediate products.

4-Methylphthaliminoglycine ester, $C_6H_3Me \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} N \cdot CH_2 \cdot CO_2Et$, prepared by the action of ethyl chloroacetate on potassium methylphthalimide, crystallises from hot water and melts at 97°.

The free *acid* is best prepared by heating methylphthalic anhydride with glycine; it crystallises from hot water in colourless needles and melts at 193—194°; the *silver* salt forms a white precipitate and the *copper* salt minute, felted needles; the acid prepared by this method may be used conveniently as a source of the ester.

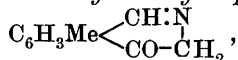
By the action of sodium methoxide, the ester is caused to undergo isomeric change, the ethyl group at the same time being replaced by methyl. *Methyl 4-oxy-7-methylisocarbostyryl-3-carboxylate*,



crystallises from methyl alcohol in colourless needles and melts at 210° to a dark liquid; the dilute alcoholic solution shows a violet-blue fluorescence. 4-Oxy-7-methylisocarbostyryl, $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix}$, pre-

pared by heating the ester with 50 per cent. sulphuric acid, separates from hot water, acetone, or alcohol in red crystals. Phosphorus oxychloride converts it into 1-chloro-4-oxy-7-methylisoquinoline,

$\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{CCl} \cdot \text{N} \\ \text{CO} \cdot \text{CH} \end{smallmatrix}$, which crystallises from acetic acid and is reduced by hydriodic acid at 180° to 4-oxy-7-methylisoquinoline,

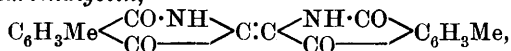


which crystallises from hot water in minute, felted needles and melts

at 162° . 1-Chloro-7-methylisoquinoline, $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{CCl} \cdot \text{N} \\ \text{CH} \cdot \text{CH} \end{smallmatrix}$, prepared

by the action of phosphorus oxychloride on the preceding compound, is a yellow oil, which gives a *picrate* melting at 141° . It is reduced by phosphorus and hydriodic acid to 7-methylisoquinoline, $\text{C}_9\text{NH}_6\text{Me}$, which solidifies to a white mass, melts at 66° , and has a characteristic odour resembling that of *isoquinoline*; the *picrate* melts at 197° , the *chromate* at 126° , the *platinichloride* with decomposition at 225° . The compound differs widely from 6-methylisoquinoline, and the alternative formulæ corresponding with the latter position of the methyl group are therefore excluded.

Dimethylcarbindicotin,



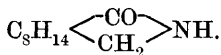
prepared by atmospheric oxidation or by the action of chromic acid on 4-oxy-7-methylisocarbostyryl, crystallises from nitrobenzene in small, reddish-brown needles with a green, metallic lustre.

7-Methylphthalonimide, $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{CO} \end{smallmatrix}$, prepared by oxidising the oxyisocarbostyryl with fuming nitric acid, crystallises from 50 per cent. alcohol in feathery needles and melts at 213° . It is hydrolysed by alkalis to *methylphthalonamic acid*, $\text{NH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO} \cdot \text{CO}_2\text{H}$, which is converted by hypochlorites into 6-methylisatin, which crystallises from hot water in red needles, melts at 169° , gives the indophenine reaction, and is isomeric with Meyer's *p*-methylisatin (Abstr., 1884, 47).

Methylphthalonic acid, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO} \cdot \text{CO}_2\text{H}$ [1 : 4 : 2], prepared from methylphthalonimide by the action of concentrated hydrochloric acid, separates from hot water in colourless crystals and melts at 103° ; the insoluble *silver* salt was analysed. The *phenylhydrazone*, $\text{C}_{16}\text{H}_{14}\text{O}_4\text{N}_2$ [or possibly its anhydride, $\text{C}_{16}\text{H}_{12}\text{O}_3\text{N}_2$], prepared by the action of phenylhydrazine hydrochloride on the acid, crystallises in yellow needles and melts with frothing at 213° . T. M. L.

The Camphidones. JULIUS TAFEL and HEINRICH BUBLITZ (*Ber.*, 1905, 38, 3806—3812).— α -Camphidone has been converted through the nitroso-compound into a campholide identical with that obtained by Baeyer and Villiger (Abstr., 1900, i, 133) by oxidising camphor

with persulphuric acid. If, therefore, camphor and the campholide are written $C_8H_{14} \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}$ and $C_8H_{14} \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} O$, α -camphidone has the formula $C_8H_{14} \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} NH$, and β -camphidone the formula



Nitroso- α -camphidone, $C_8H_{14} \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} N \cdot NO$, crystallises from light petroleum, melts at 127° , and is considerably more stable than nitroso-pyrrolidone, although it decomposes when distilled. Boiling potassium hydroxide converts it into an *acid*, probably $CH_2 \cdot C_8H_{14} \cdot CO_2H$, which melts at 149 — 155° , and when the latter is distilled it is converted into a campholide identical with that derived from camphor; in each case the crude substance appears to be a mixture, probably with a polymeric lactone, but identical products were obtained by crystallising from concentrated hydriodic acid.

Nitroso- β -camphidone, $C_8H_{14} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix} N \cdot NO$, crystallises from light petroleum in long, glistening, yellow needles and melts at 158° . It is about as stable as the α -isomeride, and, when decomposed by potassium hydroxide, yields a similar mixed campholide, from which, however, none of Baeyer and Villiger's product could be isolated.

Di- β -camphidone anhydride, $C_{20}H_{32}ON_2$, prepared by heating β -camphidone with phosphorus oxychloride, melts at 144 — 145° , has $[\alpha]_D + 207.4^\circ$ in benzene at 20° , dissolves readily in organic solvents and in mineral acids, but is reprecipitated from the latter by sodium acetate; the yield is good, and as α -camphidone does not give an anhydride, the use of phosphorus oxychloride affords a convenient method of separating the isomerides. When dissolved in acetic acid, the anhydride readily yields a *bromide* which crystallises from acetic acid in orange-yellow scales, melts at 196° , and is decomposed again by the action of acetone.

T. M. L.

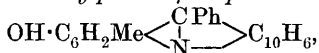
Syntheses of Aminonaphthacridines. FRITZ ULLMANN and EMIL BÜHLER (*Zeit. Farb. Text. Ind.*, 1905, 4, 521—522. Compare Ullmann and Naef, *Abstr.*, 1900, i, 361; Ullmann and Torre, *Abstr.*, 1904, i, 929).—9-Amino-1:2-phenonaphthacridine has been prepared by the following methods. The percentages given are the relation of the yield obtained to the theoretical. (1) A mixture of *m*-tolylenediamine hydrochloride, sulphur, and β -naphthol is heated at 180 — 190° (19.4 per cent.). (2) Dihydroxydinaphthyl disulphide and *m*-tolylenediamine are heated with β -naphthol at 180 — 190° (20 per cent.). (3) Anhydroformaldehyde-*m*-phenylenediamine is treated with β -naphthol (10.7 per cent.). (4) β -Naphthol, *m*-phenylenediamine, and trioxymethylene are fused together and the product distilled rapidly (24.4 per cent.). (5) β -Naphthol and *m*-phenylenediamine are heated with dihydroxydinaphthylmethane (18.6 per cent.).

The orange-yellow, aqueous solution of 9-amino-1:2-phenonaphthacridine dyes tannin mordanted cotton-wool clear orange-yellow shades;

the *nitrate*, $C_{17}H_{12}N_2, HNO_3$, crystallises in red needles and is less soluble than the hydrochloride in water.

Dihydroxydinaphthyl disulphide is obtained in a yield of 88.1 per cent. of the theoretical when lead oxide is added to a solution of β -naphthol and sulphur in nitrobenzene at 160—170°. G. Y.

Hydroxyacridines. FRITZ ULLMANN and ROBERT FITZENKAM (*Ber.*, 1905, 38, 3787—3796. Compare Ullmann, Racovitza, and Rozenband, *Abstr.*, 1902, i, 240; Ullmann, Rozenband, Mühlhauser, and Grether, *ibid.*; Ullmann and Grether, *Abstr.*, 1903, i, 447).—10-Hydroxy-7-phenyl-9-methylpheno- $\alpha\beta$ -naphthacridine,



is formed by heating 9-amino-12-phenyl-10-methylpheno- $\alpha\beta$ -naphthacridine with 10 per cent. sulphuric acid at 200—210° under pressure for eight hours, or, together with its leuco-base, by warming *p*-amino-*o*-cresol with benzaldehyde and heating the resulting benzylidene compound with β -naphthol at 210—220°. It crystallises from aniline or nitrobenzene in yellowish-brown needles, melts above 360°, and dissolves in alcoholic hydrogen chloride to form a brownish-red solution, in alcoholic sodium hydroxide to form a yellow solution, or in concentrated sulphuric acid to form a yellowish-brown solution with dark green fluorescence; the base is precipitated on dilution of its solution in glacial acetic acid; the *hydrochloride* forms steel-blue, glistening needles and melts and decomposes at about 330°.

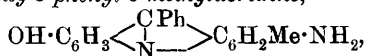
The *leuco-base* is obtained as a slightly yellowish-brown powder, which does not melt at 350°; it is oxidised to the phenonaphthacridine by ferric chloride in acetic acid solution.

p-Nitro-*o*-cresol is best prepared by diazotising nitrotoluidine in 10 per cent. sulphuric acid at 0° and pouring the product into boiling dilute sulphuric acid. When shaken with methyl sulphate and aqueous sodium hydroxide, it forms the *methyl ether*, $OMe \cdot C_6H_3Me \cdot NO_2$, which crystallises in yellow needles, melts at 71°, and on reduction with stannouschloride and alcoholic hydrochloric acid yields the *stannichloride*, $(C_8H_{11}ON)_2, 2HCl, SnCl_4$, crystallising in colourless needles. The free base, $NH_2 \cdot C_6H_3Me \cdot OMe$, crystallises in long needles, melts at 55°, and boils at 250—252°. The *hydrochloride*, $C_8H_{11}ON, HCl$, crystallises in glistening, almost colourless needles and melts at 269—270°. The *acetyl* derivative, $C_8H_{10}ONAc$, crystallises in small, colourless leaflets and melts at 132°.

When heated with benzaldehyde and β -naphthol at 220°, *p*-amino-*o*-cresol methyl ether forms 10-methoxy-7-phenyl-9-methyl-7:12-dihydropheno- $\alpha\beta$ -naphthacridine, $OMe \cdot C_6H_2Me \left\langle \begin{array}{c} CHPh \\ | \\ NH \end{array} \right\rangle C_{10}H_6$, which is obtained as a colourless, crystalline powder, melts at 232—234°, and forms colourless solutions with blue fluorescence. 10-Methoxy-7-phenyl-9-methylpheno- $\alpha\beta$ -naphthacridine, $C_{25}H_{19}ON$, is obtained at the same time, and it is also formed by oxidation of the leuco-base with ferric chloride in acetic acid solution, or with bromine in carbon tetrachloride solution; it crystallises in glistening, yellow leaflets, melts at 205—206°, and dissolves in dilute acids or organic solvents to

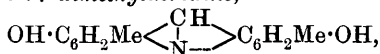
form yellow solutions with bluish-green fluorescence. The *picrate* forms a yellow, crystalline powder; the *nitrate*, $C_{25}H_{19}ON, HNO_3$, crystallises in golden prisms and melts at 224° .

2-Amino-8-hydroxy-5-phenyl-3-methylacridine,



is formed together with the dihydroacridine when phenyltetra-aminoditolylmethane is heated with resorcinol at $165-185^\circ$, or by oxidation of the leuco-base with ferric chloride. It crystallises from aniline or alcohol in glistening, orange needles, melts at $368-373^\circ$, and dissolves in dilute sodium hydroxide, dilute acids, or concentrated sulphuric or glacial acetic acid, forming yellow solutions with green fluorescence. The *hydrochloride* forms yellowish-brown crystals and is dissociated by water; the *acetate*, $C_{20}H_{16}ON_2, C_2H_4O_2$, crystallises in glistening, orange, hygroscopic needles, melts and decomposes at $187-193^\circ$, and in aqueous solution dyes tannin mordanted cotton-wool yellow. The *leuco-base*, $C_{20}H_{18}ON_2$, forms an almost colourless powder, melts at $305-311^\circ$, and dissolves in alcohol containing traces of an alkali hydroxide.

2:8-Dihydroxy-3:7-dimethylacridine,

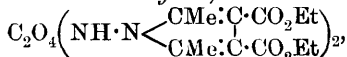


is formed by heating tetra-aminoditolylmethane with sulphuric acid at 220° under pressure. It crystallises from nitrobenzene in small, yellowish-brown needles and melts above 360° ; the *sodium* derivative, $C_{15}H_{12}O_2NNa$, crystallises in orange needles and dissolves in water or alcohol to form yellow solutions with green fluorescence. The *diacetyl* derivative, $C_{19}H_{17}O_4N$, crystallises in glistening prisms, melts at 202° , and is hydrolysed by dilute acids or alkali hydroxides. The *dibenzoyl* derivative, $C_{29}H_{21}O_4N$, crystallises in yellow leaflets, melts at 258° , and forms the *hydrochloride*, $C_{29}H_{21}O_4N, HCl$, crystallising in yellow needles and melting at $280-285^\circ$.
G. Y.

Coloured and Colourless Di-imines. FRIEDRICH KEHRMANN (*Ber.*, 1905, 38, 3777—3778. Compare Willstätter and Pfannenstiel, *Abstr.*, 1905, i, 669; Pringsheim, *ibid.*, i, 934).—The author considers that there is no evidence to support the suggestion that there are two series of quinonedi-imine salts, but that many of the deeply-coloured oxidation derivatives of amines are of the nature of quinhydrone.

G. Y.

Condensation Products of Oxalylhydrazide. I. CARL BÜLOW (*Ber.*, 1905, 38, 3914—3917. Compare *Abstr.*, 1903, i, 196; Bülow, Riess, and Sautermeister, *Abstr.*, 1905, i, 660).—*Ethyl 1-oxamidobis-2:5-dimethylpyrrole-3:4-dicarboxylate,*



is formed by the condensation of oxalylhydrazide (Curtius, Schöfer, and

Schwan, Abstr., 1895, i, 264) with ethyl diacetylsuccinate in boiling acetic acid solution. It crystallises in leaflets, melts at 291—293°, is soluble in boiling nitrobenzene, dissolves without change in dilute alkali hydroxides or aqueous ammonia, from which it is precipitated by the action of carbon dioxide, and separates unchanged from its solution in concentrated sulphuric acid when poured on to ice. When heated above its melting point, the *acid* obtained on hydrolysis of the ester yields

1-oxamidobis-2 : 5-dimethylpyrrole, $C_2O_4(NH \cdot N \begin{smallmatrix} \text{CMe:CH} \\ \text{CMe:CH} \end{smallmatrix})_2$, which is

formed also by the condensation of oxalylhydrazide with acetylacetone in glacial acetic acid solution. It crystallises in glistening, white leaflets, dissolves readily in boiling alcohol, acetone, or dilute alkali hydroxides, is precipitated by carbon dioxide from its alkaline solution, and gives the pine-wood and Laubenheimer's pyrrole reactions. G. Y.

Action of 2 : 5-Dimethylpyrazine on Aldehydes. R. FRANKE (*Ber.*, 1905, 38, 3724—3728).—2-Styryl-5-methylpyrazine, $C_{13}H_{12}N_2$, and 2 : 5-distyrylpyrazine, $C_{20}H_{16}N_2$, obtained by the condensation of 2 : 5-dimethylpyrazine and benzaldehyde with zinc chloride at 200°, may be separated by distillation with steam. Styrylmethylpyrazine distils over slowly, and after several crystallisations from alcohol forms colourless, glistening plates melting at 90°, and yields a *picrate*, $C_{19}H_{15}O_7N_5 \cdot 4H_2O$, melting at about 132°. Distyrylpyrazine is not volatile with steam, and crystallises from a mixture of benzene and light petroleum in sulphur-yellow, glistening plates melting at 219°. The *hydrochloride*, $C_{20}H_{16}N_2 \cdot HCl$, forms red crystals; the *platini-chloride* also forms reddish-yellow crystals and melts at 219°. The *picrate* is unstable and melts at 165°. Attempts to reduce the distyryl derivative were not successful.

2 : 5-Di- $\gamma\gamma\gamma$ -trichloropropenylpyrazine, obtained by the action of chloral on dimethylpyrazine at the ordinary temperature, crystallises with $4H_2O$ in compact prisms, melts at 89°, and dissolves readily in alcohol.

Di-*p*-methylstyrylpyrazine, $C_{22}H_{20}N_2$, obtained from 2 : 5-dimethylpyrazine, *p*-tolualdehyde, and zinc chloride at 170° in an oil-bath, crystallises from benzene and melts at 238°. The *hydrochloride*, $C_{24}H_{20}N_2 \cdot HCl \cdot \frac{1}{2}H_2O$, crystallises in small, pale red needles, becomes yellow at 160°, and melts at 240°. The *mercurichloride*,

$(C_{22}H_{20}N_2)_2HgCl_2$, melts at 231° and the *platini-chloride* at 206°.

Di-*p*-methoxystyrylpyrazine, $C_{22}H_{20}O_2N_2$, crystallises from benzene or chloroform in yellow plates and melts at 235°. The *mercurichloride*, $C_{22}H_{20}O_2N_2 \cdot HCl \cdot HgCl_2 \cdot 3H_2O$, melts at 96°. The *picrate* crystallises from chloroform in bright red crystals, $C_{22}H_{20}O_2N_2 \cdot C_6H_3O_7N_3 \cdot 2CHCl_3$, melting at 217°.

2-o-Hydroxystyryl-5-methylpyrazine, $C_{13}H_{12}ON_2$, obtained from dimethylpyrazine, salicylaldehyde, and zinc chloride at 170—180°, melts at 228° and dissolves readily in alcohol and glacial acetic acid; the *picrate* melts at 227°.

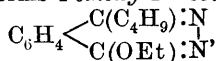
2-*p*-Nitrostyryl-5-methylpyrazine, $C_{13}H_{11}O_2N_3$, forms a yellow powder

melting at about 174°. The *platinichloride* decomposes at about 200°. J. J. S.

Condensation of Ethyl Acetoacetate with Phenylmethylpyrazolone. ROBERT STOLLE (*Ber.*, 1905, 38, 3856. Compare Abstr., 1905, i, 838).—The lactone constitutional formula ascribed to the condensation product of ethyl acetoacetate and phenylmethylpyrazolone has already been put forward by G. Cohn [Tabular summary of the Pyrazole derivatives]. E. F. A.

1-isoButylphthalazine. HANS WÖBLING (*Ber.*, 1905, 38, 3925—3928).—When reduced with zinc and fuming hydrochloric acid, 1-isobutylphthalazone (Bromberg, Abstr., 1896, i, 579) yields 1-isobutylphthalimidine, $C_6H_4 \begin{smallmatrix} \text{CH}(C_4H_9) \\ \text{CO} \end{smallmatrix} NH$, which forms colourless, glistening crystals and melts at 153°.

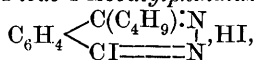
On slow evaporation of its ethereal solution, 4-chloro-1-isobutylphthalazine (Bromberg, *loc. cit.*) crystallises in transparent, doubly-refracting needles melting at 38°. When boiled with sodium ethoxide in alcoholic solution, it forms 4-ethoxy-1-isobutylphthalazine,



which is obtained as an oil having an odour of hyacinths; the *sulphate*, $(C_{14}H_{18}ON_2)_2 \cdot H_2SO_4$, crystallises from alcohol and melts at 109°.

4-Phenoxy-1-isobutylphthalazine, $C_6H_4 \begin{smallmatrix} C(C_4H_9):N \\ C(OPh):N \end{smallmatrix}$, formed by heating 4-chloro-1-isobutylphthalazine with sodium phenoxide in phenol, crystallises in white needles and melts at 108°.

When warmed with hydriodic acid of sp. gr. 1.70, 4-chloro-1-isobutylphthalazine yields 4-iodo-1-isobutylphthalazine hydriodide,



which crystallises in glistening, orange, doubly-refracting needles and melts at 127°.

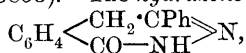
The action of boiling hydriodic acid of sp. gr. 1.70, in presence of red phosphorus, on 4-chloro-1-isobutylphthalazine leads to the formation of 1-isobutylphthalazine, ammonia, isobutylphthalazone, and isobutyldihydroisindole.

1-isoButylphthalazine, $C_6H_4 \begin{smallmatrix} C(C_4H_9) \\ CH=N \end{smallmatrix} N$, is obtained as an oil which is soluble in mineral acids; the *platinichloride*, $(C_{12}H_{14}N_2)_2 \cdot H_2PtCl_6$,

melts at 157°; the *hydriodide* crystallises in brown leaflets and decomposes at about 100°; the *aurichloride* crystallises in yellow needles, melts at 137°, and decomposes at about 183°; the *dichromate*, $(C_{12}H_{14}N_2)_2 \cdot H_2Cr_2O_7$, is obtained as a red, crystalline precipitate; the *ferrocyanide*, $(C_{12}H_{14}N_2)_2 \cdot H_4Fe(CN)_6$, forms a yellow, voluminous precipitate and decomposes at high temperatures without melting.

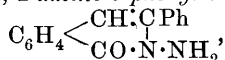
G. Y.

Action of Hydrazine on β -Deoxybenzoin-*o*-carboxylic Acid and on its Lactone (3-Phenylisocoumarin). HANS WÖBLING (*Ber.*, 1905, 38, 3845—3853).—The *hydrazone anhydride*,



prepared by the action of hydrazine hydrate on β -deoxybenzoin-*o*-carboxylic acid, crystallises in long, colourless needles melting at 202°. The *methyl* derivative, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \cdot \text{CPh} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{NMe} \end{array} \text{N}$, crystallises in long, colourless, glistening, asbestos-like needles melting at 133°; the corresponding *ethyl* derivative forms colourless needles melting at 142°.

The *nitroso*-derivative, $\text{C}_{15}\text{H}_{11}\text{O}_2\text{N}_3$, separates in clear, doubly-refracting crystals which melt and decompose at 110°. On reduction with zinc and hydrochloric acid, the hydrazone anhydride is converted into *isobenzylidenephthalimidine*. On warming it with phosphorus oxychloride, an isomeride, *2-amino-3-phenylisocarbostyryl*,



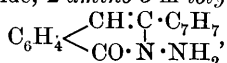
is formed, crystallising in brown, monoclinic leaflets melting at 131°. The *nitroso*-derivative, crystallising in needles which sinter at 230° and melt at 240°, proved to be identical with *nitroisobenzylidenephthalimidine*. On condensation with benzaldehyde, *2-benzylidene-amino-3-phenylisocarbostyryl*,

$\text{C}_6\text{H}_4 \begin{array}{c} \text{CH} \cdot \text{CPh} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{N} \cdot \text{N} \cdot \text{CHPh} \end{array}$, is formed, which separates in green crystals melting at 116° to a bright green liquid.

By the interaction of deoxybenzoic acid and hydrazine in presence of a large excess of an alkali hydroxide, a compound $\text{C}_{30}\text{H}_{24}\text{O}_4\text{N}_2$ is formed, which crystallises in doubly-refracting, microscopic, citron-yellow needles and melts at 226°; this forms a dibasic *silver* salt. E. F. A.

Action of Hydrazine on *m*-Tolylisocoumarin. ALBERT LIECK (*Ber.*, 1905, 38, 3853—3856).—*m*-Methylstilbene-*o*-carboxylic acid, $\text{C}_7\text{H}_7 \cdot \text{CH} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, is obtained from *m*-xylidenephthalide by conversion first into *m*-methyldeoxybenzoic acid, reduction of this by sodium amalgam, and dehydration of the hydroxy-acid so obtained by heating for one hour at 215°. It crystallises in thin, yellowish-white leaflets melting at 158°; the *silver* salt forms a voluminous, colourless precipitate.

By the action of hydrazine hydrate on *m*-tolylisocoumarin a *hydrazone anhydride*, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \cdot \text{C}(\text{C}_7\text{H}_7) \\ \diagup \quad \diagdown \\ \text{CO} \text{---} \text{NH} \end{array} \text{N}$, is formed, crystallising in snow-white, obliquely cut plates which sinter at 175° and melt from 190—191°. On heating with 20 per cent. hydrochloric acid, it is converted into an isomeride, *2-amino-3-m-tolylisocarbostyryl*,

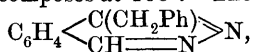


which forms colourless crystals melting at 98—99°. This condensation could not be effected by using phosphorus oxychloride (compare

Wölbling, preceding abstract), nor will methyl isocoumarin undergo the hydrazone anhydride condensation. E. F. A.

Phthalazines. ALBERT LIECK (*Ber.*, 1905, 38, 3918—3924).—4-Iodo-1-benzylphthalazine, $C_{15}H_{11}N_2I$, is formed by heating 4-chloro-1-benzylphthalazine (Gabriel and Neumann, *Abstr.*, 1893, i, 346) with hydriodic acid boiling at 127° ; it crystallises in long, white needles, becomes yellow at 100° , and finally reddish-brown at 146° , when it melts and decomposes.

Prolonged action of hydriodic acid on 4-chloro-1-benzylphthalazine in presence of red phosphorus leads to the formation of 1-benzylphthalazine hydriodide, $C_{15}H_{12}N_2HI$, which crystallises in yellow, rhombic leaflets and decomposes at 100° . The base,

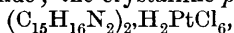


crystallises in white, rectangular plates and melts at $81-82^\circ$. The picrate, $C_{15}H_{12}N_2 \cdot C_6H_3O_7N_3$, crystallises in yellow needles and melts at 146° ; the *platinichloride* forms a yellowish-brown, crystalline mass.

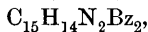
When warmed with aniline, 4-chloro-1-benzylphthalazine forms 4-anilino-1-benzylphthalazine, $C_{21}H_{17}N_3$, which crystallises in white hexahedra and melts at 180° .

Oxidation of 1-benzylphthalazine with potassium permanganate in alkaline solution leads to the formation of 1-benzoylphthalazine, $C_8H_5N_2Bz$, which crystallises in matted, white needles, melts at $123-124^\circ$, and is readily soluble in the ordinary organic solvents; the yellow, crystalline *platinichloride*, $(C_{15}H_{10}ON_2)_2 \cdot H_2PtCl_6$, melts and decomposes at 258° . The *oxime*, $C_8H_5N_2 \cdot CPh \cdot NOH$, crystallises in sheaves of white prisms, melts to a reddish-brown liquid at $243-244^\circ$, and is readily soluble in dilute sodium hydroxide or hydrochloric acid, separating from its solution in the latter as the *hydrochloride* in delicate, white needles.

When reduced with sodium amalgam, 1-benzylphthalazine yields 1-benzyltetrahydrophthalazine, $C_{15}H_{16}N_2$, which is obtained as an oil; the *hydrochloride*, $C_{15}H_{16}N_2 \cdot HCl$, decomposes at $190-200^\circ$, is easily soluble in hot water or dilute hydrochloric acid, and reduces Fehling's solution and mercuric oxide; the crystalline *platinichloride*,



commences to decompose at 180° . The *dibenzoyl* derivative,



crystallises in long, yellow plates and melts at $135-136^\circ$.

4-Chloro-1-phenylphthalazine, $C_{14}H_9N_2Cl$, formed by the action of phosphorus oxychloride on 1-phenylphthalazone, crystallises in glistening, white leaflets, melts at $160-161^\circ$, is readily soluble in warm xylene, alcohol, toluene, or glacial acetic acid, and when heated with hydriodic acid, boiling at 127° , yields 4-iodo-1-phenylphthalazine, $C_{14}H_9N_2I$, which crystallises from alcohol in matted, long, white needles, becomes yellow at 120° , and melts and decomposes at $188-189^\circ$. When boiled with hydriodic acid and red phosphorus in a reflux apparatus, 4-chloro-1-phenylphthalazine yields 1-phenylphthalazine hydriodide, which separates in yellow needles and decomposes at $170-180^\circ$. The base, $C_{14}H_{10}N_2$, crystallises in white prisms, melts at

142—143°, and is easily soluble in most organic solvents; the *platini-chloride* forms orange-yellow crystals and melts and decomposes at 223°; the yellow, crystalline *picrate*, $C_{20}H_{13}O_7N_5$, melts at 180°.

4-*Anilino-1-phenylphthalazine*, $C_{20}H_{15}N_3$, obtained by warming 4-chloro-1-phenylphthalazine with aniline, crystallises in needles and melts at 231°.

1-*Phenyltetrahydrophthalazine* is obtained on reduction of 4-chloro-1-phenylphthalazine with sodium amalgam as an almost colourless, aromatic syrup, which distils slowly in a current of steam; the *hydro-chloride*, $C_{14}H_{14}N_2 \cdot HCl$, forms white needles, commences to decompose at 220°, is melted at 250°, and reduces Fehling's solution and mercuric oxide; the *picrate* is obtained as a yellow emulsion which crystallises when rubbed; the *platinichloride*, $(C_{14}H_{14}N_2)_2 \cdot H_2PtCl_6$, crystallises in leaflets and decomposes at 140°. The *dibenzoyl* derivative, $C_{28}H_{22}O_2N_2$, crystallises in long, slightly yellow prisms and melts at 158—159°.

G. Y.

New Mode of Formation of Di-*p*-aminodiphenylamine.

PHILIPPE BARBIER and PAUL SISLEY (*Bull. Soc. chim.*, 1905, [iii], 33, 1232—1234. Compare following abstract).—*p*-Aminozobenzene hydrochloride is added to a saturated solution of sulphur dioxide in water, and to this zinc dust is gradually added until complete decolorisation is effected. The liquid is then poured into excess of sulphuric acid, diluted with its own volume of water, and the mixture boiled. On cooling, crystals of di-*p*-aminodiphenylamine sulphate separate. From this the base may be liberated with sodium carbonate. It crystallises from boiling water in small needles with a violet tint and melts at 157—158°.

The aminoazo-derivative of *o*-toluidine can be converted by the same method into the corresponding di-*p*-amino-base.

T. A. H.

s- and *as*-Phenosafranines. PHILIPPE BARBIER and PAUL SISLEY (*Bull. Soc. chim.*, 1905, [iii], 33, 1190—1198. Compare Abstr., 1905, i, 840).—Commercial phenosafranine, prepared by oxidising a mixture of 2:4'-diaminodiphenylamine and aniline, contains *s*-phenosafranine,

$NH_2 \cdot C_6H_3 \begin{array}{c} \diagup N \\ \diagdown \end{array} C_6H_3 : NH$, which it is proposed to name *indopheno-*

safrafranine, and *as*-phenosafranine, $NH_2 \cdot C_6H_4 \cdot N \begin{array}{c} C_6H_4 \cdot N \\ | \end{array} C_6H_3 : NH$, which

it is proposed to call *azophenosafrafranine*. The former was prepared from commercial safranin by repeated crystallisation from dilute hydrochloric acid, the hydrochloride of the *as*-isomeride being the less soluble. *s*-Phenosafrafranine was prepared by oxidising a mixture of di-*p*-aminodiphenylamine (1 mol.) with aniline (1 mol.), and was purified by repeated crystallisation of the hydrochloride from dilute hydrochloric acid.

Azophenosafrafranine hydrochloride, $C_{18}H_{15}N_4Cl \cdot 3H_2O$, crystallises in dull green lamellae which exhibit little or no metallic lustre; it becomes anhydrous at 120—130°, and in this state is hygroscopic. One litre of water dissolves 12.88 grams of the salt at 24°. The *free base* may be

obtained by adding sodium hydroxide to an aqueous solution of the hydrochloride; it separates from water in small, green crystals, which are heavier than those of indophenosafranine. A litre of water dissolves 0.58 gram and a litre of alcohol (90°) 18.08 grams of the base at 20°.

Indophenosafranine hydrochloride, $C_{18}H_{15}N_4Cl \cdot \frac{1}{2}H_2O$, forms hard, granular crystals, which exhibit a brilliant metallic lustre; it becomes anhydrous at 120—130°, and is then hygroscopic. One litre of water dissolves 5.5 grams of the salt at 24°. The *free base* separates from water in green lamellæ having a well-marked metallic lustre. A litre of water dissolves 2.23 grams, and a litre of alcohol (90°) 9.09 grams of the base at 20°.

Measurements of the electrical conductivities of aqueous solutions of the two hydrochlorides show that for equal concentrations the azophenosafranine salt is a better conductor than its isomeride, and this divergence increases with greater dilution, the conductivity of the indophenosafranine salt remaining fairly constant, whilst that of its isomeride increases.

The absorption of light by aqueous solutions of the two salts is qualitatively the same, and ranges from the middle of the green to the beginning of the indigo, with a maximum where the green passes into the blue. Indophenosafranine hydrochloride shows a greater absorption than the isomeric salt except for light $\mu = 549$. T. A. H.

[A New Method of Formation of Diazo-compounds and a General Method for determining the Constitution of Azo-dyes.] OTTO SCHMIDT (*Ber.*, 1905, 38, 4022—4023).—The author had overlooked in his recent paper (*Abstr.*, 1905, i, 951) the earlier work (Meldola and Morgan, *Trans.*, 1889, 55, 608; Meldola and Hanes, *ibid.*, 1894, 65, 841; Meldola and Southerden, *Proc.*, 1894, 10, 118) in this connection. W. A. D.

Examination of Proteid Preparations. PETER BERGELL (*Chem. Centr.*, 1905, ii, 1103—1104; from *Med. Klin.*, 1, 1042—1045).—The examination of a proteid preparation is described for the case of gliadin, which is obtained from the best wheat meal by a purely mechanical method which depends mainly on a centrifugal process. In the dough thus prepared, 87.85 per cent. of the proteids, 90 of the fats, and 64.4 of the mineral substances of the original meal are present. After washing, drying, and grinding to an extremely fine powder, the air-dried substance contains 1.35 per cent. of nitrogen, 9.8 of water, and 6.2 of substances soluble in alcohol (lecithin), and yields 0.52 of ash. After completely extracting with alcohol, the residue contains 49.32 per cent. of carbon, 7.27 of hydrogen, 16.15 of nitrogen, and 0.701 of sulphur.

[With TH. DÖRPINGHAUS.]—When hydrolysed, the pure substance yields 1.2 per cent. of humin substances, 34.17 of glutamic acid, and rather less than 1 of tyrosine. About 5 per cent. of the nitrogen is present in the form of diamino-acids. The hydrolysis shows that two-thirds of the weight of the substance consists of monoamino-acids and

that these acids contain 60 per cent. of the carbon of the gliadin. Alanine, leucine, pyrrolidine-2-carboxylic acid, phenylalanine, aspartic acid, and glycollic acid were also isolated. Gliadin is distinctly peptonised by the action of highly active gastric juice of dogs and is also directly attacked by pancreatin.

Clinical experiments on gliadin and its preparations are also described in the original paper. E. W. W.

Artificial Change of Albumin into Globulin. LEOPOLD MOLL (*Beitr. chem. Physiol. Path.*, 1905, 7, 311—312. Compare Abstr., 1904, i, 356).—Further details in support of the author's previous contention that the naturally occurring pseudo-globulin of horse's blood is identical with that prepared artificially from the crystallised albumin of the same blood. W. D. H.

The Monoamino-acids of Crystallised Egg-albumin. EMIL ABDERHALDEN and FRITZ PREGL (*Zeit. physiol. Chem.*, 1905, 46, 24—30).—The following products were separated out and estimated; the numbers given are the amounts obtained from 100 grams of ash-free, crystallised egg-albumin: alanine, 2.1; leucine, 6.1; pyrrolidine-2-carboxylic acid, 2.25; aspartic acid, 1.5; glutamic acid, 8.0; phenylalanine, 4.4; tyrosine, 1.1; and cystine, 0.2 grams. W. D. H.

Artificial Digestion Experiments. EDWARD GUDEMAN (*J. Amer. Chem. Soc.*, 1905, 27, 1436—1442).—A series of experiments has been made with the object of ascertaining the influence of the following substances on the artificial digestion of egg-albumin with pepsin or pancreatin. Salicylic, benzoic, boric, and sulphurous acids, "saccharin," sugar, vinegar, ethyl and methyl alcohols, sodium chloride, formaldehyde, smoke, "condensed smoke," creosote, hydrochloric, sulphuric, phosphoric and nitric acids, sodium salicylate, benzoate, sulphite, borate and carbonate, and sodium hydrogen sulphite. The results are tabulated. In an acid medium, the only preservatives or condiments which retarded the digestion when present in a proportion of 1 : 400 or less were salicylic acid, formaldehyde, smoke, "condensed smoke," and creosote. Salicylic acid did not retard the digestion when present in the proportion of 1 : 1000. Acid substances, when added to a neutral solution of the albumin, accelerated the digestion, which then proceeded normally as in an acid medium. On the other hand, the addition of alkaline preservatives to a neutral medium caused abnormal results, the action of the ferment being retarded. In an alkaline medium, preservatives and condiments were found to retard the digestion to an extent depending on the degree of alkalinity.

A similar series of experiments was carried out with various coloured substances and dyes. The results showed that of the various colouring matters tested, only ultramarine, burnt sienna, chrome yellow, and ponceau 2R affected artificial digestion with pepsin when present in the proportion of 1 : 400 or less. The synthetical colouring

matters were found to be less active than animal or mineral colours and not more active than vegetable colouring matters. Vegetable and synthetical colouring matters are directly digested by pepsin and pancreatin.

E. G.

Fibrinoglobulin. W. HUISKAMP (*Zeit. physiol. Chem.*, 1905, 46, 273—279. Compare Abstr., 1905, i, 499).—Polemical. The author maintains the correctness of his views on the fibrinoglobulin question in spite of the criticisms of Heubner (Abstr., 1905, i, 725).

W. D. H.

Decomposition of Casein by means of Ozone. CARL D. HARRIES (*Ber.*, 1905, 38, 2990—2992).—The action of ozone on casein in *N*/10 sodium hydroxide solution leads to the formation of a colourless, slightly acid solution, which contains nitrous and nitric acids, has only a slight reducing action on Fehling's solution, and does not contain hydrogen peroxide; after some time, it acquires a characteristic odour of melted sugar. When boiled with phenylhydrazine hydrochloride and sodium acetate, the solution yields a yellow, flocculent *osazone*, which decomposes at about 200°, has acid properties, and reduces Fehling's solution like lactosazone, but is only sparingly soluble in water. The osazone contains practically the whole of the phosphorus from the casein.

The solution, after treatment with ozone, yields with lead acetate a white precipitate; from this there is obtained on treatment with hydrogen sulphide a white *substance* in a yield of at least 30 per cent. of the original casein, which melts and decomposes at 135°, is readily soluble in water, has an acid reaction, and yields the same osazone as is obtained directly from the ozonised solution; the white substance contains almost 2 per cent. of phosphorus, more than 40 per cent. of oxygen, and about 5—7 per cent. of nitrogen.

On removal of the lead from the filtrate from the lead acetate precipitate and evaporation in a vacuum, there is obtained a gelatinous *substance* which is readily soluble in water and gives the biuret reaction and yields a white precipitate with phosphotungstic acid.

G. Y.

Cleavage Products of Proteoses. PHOEBUS A. LEVENE (*J. Biol. Chem.*, New York, 1905, 1, 45—58).—The experiments fail to corroborate Pick's statement that heteroalbumose in contradistinction to protoalbumose contains abundant glycine and leucine, but little or no tyrosine. The most striking difference noted is in the proportion of lysine, not of arginine, as Hart stated.

W. D. H.

Protagon. EDWARD R. POSNER and WILLIAM J. GIES (*J. Biol. Chem.*, New York, 1905, 1, 59—112).—A complete and critical discussion of the protagon controversy. The present experiments confirm the statement that protagon is a mixture of substances, some of which contain phosphorus, whilst some do not. The substance phrenosin (Thudichum) is identical with that named pseudocerebrin by Gamgee,

and cerebrone by Thierfelder. It is always present in protagon. The name phrenosinic acid is suggested for Thudichum's neurostearic acid.

W. D. H.

Nature of Blood Pigments. M. PIETTRE and A. VILA (*Compt. rend.*, 1905, 141, 734—736. Compare Cazeneuve and Breteau, *Abstr.*, 1899, i, 840; ii, 440; Nencki and Sieber, *Abstr.*, 1885, 69, 825; 1900, i, 709; 1901, i, 434).—Following Nencki's method (compare *Abstr.*, 1900, i, 709), the authors have obtained crystalline acetylhæmi identical with the compound he described having the composition



if, however, the substance is prepared in a medium free from chlorides, the quantity of chlorine in the compound diminishes and the quantity of iron increases, whilst a specimen prepared from pure crystallised oxyhæmoglobin is free from chlorine and contains 9.20 per cent. of iron, Nencki's compound containing 5.44 per cent. of chlorine and 8.59 per cent. of iron. In view of these facts the authors are of opinion that the Teichmann-Nencki blood crystals do not consist of a definite chemical compound.

M. A. W.

Crystallised Hæmatin. M. PIETTRE and A. VILA (*Compt. rend.*, 1905, 141, 1041—1044. Compare preceding abstract).—Crystallised hæmatin, obtained by extracting crystalline oxyhæmoglobin with methyl alcohol containing 3 per cent. of formic acid, forms black needles with a steel-blue reflex which resemble hæmin or acetylhæmin and deviate the plane of polarised light. The absorption spectrum in acid solution shows four characteristic absorption bands having their centres at $\lambda = 630, 575, 534$, and 494 respectively; in ammoniacal solution, the two latter bands persist, but in place of the two former there is a well-marked band with centre at $\lambda = 606$.

A substance of the nature of a higher fatty acid having $C = 76.6$ and $H = 10.67$ per cent. has been obtained from crystallised hæmatin, and the same compound has been prepared similarly from amorphous hæmatin, acetylhæmin, and hæmin.

M. A. W.

[**Oxidation of Nucleic Acid.**] FRIEDRICH KUTSCHER (*Zeit. physiol. Chem.*, 1905, 46, 305—306. Compare *Abstr.*, 1905, i, 621, 725).—A reply to Burian. Polemical.

W. D. H.

Nucleic Acid of the Intestine. KATSUJI INOUE and Y. KOTAKE (*Zeit. physiol. Chem.*, 1905, 46, 201—205. Compare *Abstr.*, 1904, i, 837).—The following seven substances were identified among the cleavage products of the nucleic acid from the intestine: lævulic acid, guanine, adenine, xanthine, hypoxanthine, thymine, cytosine.

W. D. H.

The Monoamino-acids of Keratin from Horse-hair. EMIL ABDERHALDEN and H. GIDEON WELLS (*Zeit. physiol. Chem.*, 1905, 46, 31—39).—One hundred grams of ash-free, water-free, and melanin-free keratin, prepared from horse-hair, yielded, on hydrolysis, glycine, 4.7; alanine, 1.5; aminovaleric acid, 0.9; leucine, 7.1; pyrrolidine-2-carb-

oxylic acid, 3.4; aspartic acid, 0.3; glutamic acid, 3.7; tyrosine, 3.2 and serine, 0.6 grams. W. D. H.

The Monoamino-acids of Keratin from Goose Feathers. EMIL ABDERHALDEN and E. R. LE COUNT (*Zeit. physiol. Chem.*, 1905, 46, 40—46).—One hundred grams of ash-free and water-free keratin prepared from goose-feathers yielded, on hydrolysis, glycine, 2.6; alanine, 1.8; aminovaleric acid, 0.5; leucine, 8.0; pyrrolidine-2-carboxylic acid, 3.5; glutamic acid, 2.3; aspartic acid, 1.1; tyrosine, 3.6; and serine, 0.4 grams. W. D. H.

Synthesis of a Substance allied to Adrenaline. Physiological Activity of Substances indirectly related to Adrenaline. HENRY D. DAKIN (*Proc. Roy. Soc., B*, 76, 491—497, 498—503).—A more detailed account of work already published (*Proc.*, 1905, 21, 154; *Abstr.*, 1905, ii, 410). G. S.

Epinephrine [Adrenaline] Hydrate. JOHN J. ABEL and RÉNE DE U. TAVEAU (*J. Biol. Chem., New York*, 1905, 1, 1—32).—The empirical formula $C_{10}H_{13}O_3N, \frac{1}{2}H_2O$, which Abel originally assigned to epinephrine hydrate, is adhered to for reasons fully stated in the paper. There is, however, a lack of agreement in the nitrogen content of specimens prepared at different times and from different glands.

W. D. H.

The Co-enzyme of Zymase. EDUARD BUCHNER and WILHELM ANTONI (*Zeit. physiol. Chem.*, 1905, 46, 136—154).—Harden and Young (*Abstr.*, 1905, ii, 109) state that boiled yeast juice contains a co-enzyme which increase the activity of the yeast zymase. The experiments now recorded show that the favouring action of the boiled juice is due to dilution of the mixture and the presence of phosphates in the boiled juice. Lecithin also has a slight favouring action.

W. D. H.

Casein as an Acid and its Distinction from Casein altered by Rennet (Paracasein). Action of Rennet. ERNST LAQUEUR (*Beitr. chem. Physiol. Path.*, 1905, 7, 273—297).—A comparison of the properties of solutions of casein and paracasein (or, as they are usually called in English, caseinogen and casein respectively) is made, chiefly in relation to their acidity and electrical conductivity. Some modifications of the accepted theories of rennet action are suggested. The action of the ferment is believed to be in part synthetical.

W. D. H.

A Comparison between Organic and Inorganic Ferments. PETER BERGELL (*Chem. Centr.*, 1905, ii, 1310—1311; from *Zeit. Klin. Med.*, 57, 381—384).—Analogies are pointed out between enzymes and their activities and inorganic catalysing agents and their actions.

W. D. H.

Organic Chemistry.

Theory of the Grignard Reactions. RICHARD ABEGG (*Ber.*, 1905, 38, 4112—4116. Compare *Abstr.*, 1904, ii, 475).—It has been already suggested that alkyl groups are amphoteric in character; in compounds such as ethyl chloride they have electro-positive properties and, on hydrolysis, yield alcohols, whilst in metallic alkyl compounds such as zinc ethyl they have electro-negative properties and, on hydrolysis, yield hydrides (paraffins). The Grignard reactions permit of similar conclusions being drawn with reference to the electro-chemical character of other organic radicles, and nine examples of different types are discussed from this point of view. Attention is called to the close analogy between the influence of electrical polarity in determining the direction of chemical change in electrolytes and in non-electrolytes, and to the fact that evidence of feeble ionisation has been obtained in the case of a few compounds generally regarded as non-electrolytes, for example, sugar, alcohol, ethyl malonate, and oxonium compounds.

T. M. L.

Decomposition of Chloroform under the Influence of Light and Air. NICOLAAS SCHOORL and L. M. VAN DEN BERG (*Chem. Centr.*, 1905, ii, 1623; from *Pharm. Weekblad*, 42, 877—888).—Quantitative experiments have shown that when chloroform is decomposed by the action of light in the presence of an excess of oxygen, carbon dioxide, water, and chlorine are formed, but that when insufficient oxygen is present, carbon oxychloride and hydrogen chloride are produced in molecular proportion. The latter conditions usually obtain in practice.

E. W. W.

Readiness of Formation of Cyclic Compounds. PAVEL IW. PETRENKO-KRITSCHENKO and A. KONSCHIN (*Annalen*, 1905, 342, 51—59).—After surveying the known data bearing on the formation of closed rings from open chains, the conclusion is drawn that the readiness, or better the velocity, of formation of cyclic compounds from open chains depends on two factors, the work necessary to bring the open chain into a cyclic position and the work required to actually close the ring.

The velocities of the reaction between potassium hydroxide and various glycol monochlorohydrins and between dibromides and zinc dust are measured. The investigation of ethylene chlorohydrin, trimethylene chlorohydrin, γ -pentylene chlorohydrin, and δ -hexylene chlorohydrin shows that there is a marked difference in the velocity of the reaction between the α -compounds and the β -compounds, whilst the remainder of the substances investigated behave in much the same way. The velocity of decomposition of γ -pentylene chlorohydrin is slightly greater than that of the others.

The velocity of the reaction of the dibromides with zinc dust is expressed as a percentage of the material which has been decom-

posed in one hour : ethylene dibromide, 19.87 ; propylene dibromide, 20.87 ; trimethylene bromide, 2.02 ; γ -pentylene dibromide, 1.80 ; pentamethylene dibromide, 1.25 ; δ -hexylene dibromide, 1.92.

The opinion is expressed that in the case of the compounds investigated, unlike the acid compounds, the "tension" of the ring which is formed does not play an important part in determining the velocity of the reaction.

K. J. P. O.

Action of Dilute Sulphuric Acid on the Pinacone formed from Ethyl Propyl Ketone. FELIX GOLDBERGER and RUDOLF TANDLER (*Monatsh.*, 1905, 26, 1473—1485. Compare Zumpfe, Abstr., 1904, i, 291 ; Lieben, Abstr., 1905, i, 167 ; Kohn, *ibid.*).—The pinacone obtained in a yield of 28 per cent. of the theoretical, by reduction of ethyl propyl ketone with sodium and water, or in poorer yield by electrolytic reduction in dilute sulphuric acid solution, with a current density of 8 amperes per square decimetre, boils at 125—126° under 11 mm., or at 254—255° under the atmospheric pressure (Oechsner de Coninck, Abstr., 1876, i, 694). When heated with 20—30 per cent. sulphuric acid in a sealed tube at 170—180° for six hours, it yields an unsaturated hydrocarbon and an oxide.

The hydrocarbon, $\begin{array}{c} \text{CHMe} \cdot \text{CPr} \\ | \quad | \\ \text{CHMe} \cdot \text{CPr} \end{array}$ (I), is a colourless oil, which has an odour of camphor, boils at 75—76° under 11 mm. or at 194—195° under the atmospheric pressure, forms a dark, resinous additive compound with 1 mol. of bromine in carbon disulphide solution, and when oxidised with nitric acid of sp. gr. 1.5 under cooling, or with alkaline permanganate solution at 60°, yields carbon dioxide and an acid ; this is volatile with steam and forms a silver salt, $\text{C}_4\text{H}_7\text{O}_2\text{Ag}$.

The oxide, $\text{C}_{12}\text{H}_{24}\text{O}$, is a slightly yellow liquid having a burning odour, which boils at 105—106° under 11 mm. or at 225° under atmospheric pressure, and is easily soluble in ether, alcohol, or chloroform. It does not form an oxime, a sodium hydrogen sulphite additive compound, or an acetyl derivative when boiled with acetyl chloride ; it remains unchanged when boiled with sodium in an atmosphere of hydrogen, or when heated with zinc ethyl in a sealed tube at 150° for three hours, or with water under pressure at 180—200°. It must be therefore an $\alpha\gamma$ - or an $\alpha\delta$ -oxide. It is not reduced by alcohol and sodium, and does not interact with magnesium ethyl iodide ; when oxidised with alkaline permanganate solution, it yields a mixture of acids, which forms silver butyrate and a silver salt, $\text{C}_7\text{H}_{13}\text{O}_2\text{Ag}$, crystallising in white needles.

G. Y.

Synthesis in the s -Heptane- $\alpha\delta\eta$ -triol Series. JULES L. HAMONET (*Compt. rend.*, 1905, 141, 1244—1245).— $\alpha\eta$ -Dimethoxyheptane- δ -ol, $\text{OH} \cdot \text{CH}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OMe})_2$, prepared by the action of ethyl formate on the magnesium derivative of γ -iodo- α -methoxypropane (compare Abstr., 1904, i, 467), is a colourless, slightly odorous liquid with a very bitter taste, which boils at 141—142° under 21 mm. or at 246—248° under the ordinary pressure, has a sp. gr. 0.969 at 18°, and does not crystallise when cooled in a mixture of solid carbon dioxide and acetone. δ -Chloro- $\alpha\eta$ -dimethoxyheptane, $\text{C}_7\text{H}_{13}\text{Cl}(\text{OMe})_2$, prepared by the action of phosphorus trichloride on the alcohol, is a colourless,

mobile liquid with an agreeable odour, boiling at 120° under 16 mm. pressure and having a sp. gr. 1.001 at 18° . *αδγ-Tribromoheptane*, $C_7H_{13}Br_3$, prepared by heating the alcohol with acetic acid and hydrobromic acid in sealed tubes at 100° , is a viscous liquid, solidifying in a mixture of solid carbonic acid and acetone, boiling at $184-185^{\circ}$ under 19 mm. pressure, and having a sp. gr. 1.775 at 18° . *αδγ-Tri-iodoheptane*, $C_7H_{13}I_3$, obtained by the action of hydrogen iodide in the cold on the alcohol, is a slightly coloured, viscous liquid, having a sp. gr. 2.343 at 18° , which cannot be distilled without decomposition.

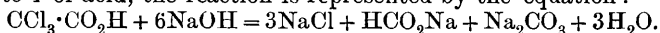
M. A. W.

Halogenated Aliphatic Acids. WILHELM LOSSEN (*Annalen*, 1905, 342, 112—155, 157—190).—It has been shown (Abstr., 1893, i, 142) that both dibromosuccinic acid and *isodibromosuccinic acid*, the latter more easily, are converted by the action of alkali hydroxides into acetylenedicarboxylic acid, a fact which is not in agreement with Wislizenus's views as to the stereoisomerism of the two dibromosuccinic acids. A new series of experiments has been undertaken with the object of throwing light on this difference.

[With ROBERT EICHLÖFF.]—Chloro- and bromo-acetic acids were converted by aqueous or alkaline solutions into glycollic acid at different temperatures, and the velocity of the hydrolysis measured. The change is accelerated by raising the temperature, and the velocity is greater in solutions containing molecular proportions of the acid and the base than in aqueous solutions. Increase, however, in the concentration of the alkali greatly hastens the velocity of the reaction. In dilute solution, the free acid decomposes far more rapidly than in concentrated solution, but in presence of alkali the reverse is the case. Bromoacetic acid under all conditions decomposes more rapidly than chloroacetic acid.

Chloroacetic acid yields not only glycollic acid but also diglycollic acid when boiled with bases, the particular reaction depending on the nature and quality of the base. Bromoacetic acid was investigated. Normal sodium hydroxide yields only glycollic acid, concentrated sodium hydroxide (1 molecule of base to 1 of acid) gives also glycollic acid, but 2 molecules of the concentrated base yield diglycollic acid and glycollic acid in the proportion of 1:2.8, and 3 molecules of the base gave the two acids in the proportion of 1:1.7. It is noteworthy that potassium hydroxide in place of sodium hydroxide increases the proportion of diglycollic acid. Barium hydroxide in neutral solution converts the bromoacetic acid into glycollic acid, but if two equivalents of the base are present for every equivalent of acid, 76 per cent. of diglycollic acid is formed.

When boiled with water, both trichloro- and tribromo-acetic acids are decomposed into chloroform and carbon dioxide. If the decomposition is effected by sodium hydroxide in the proportion of 6 molecules of base to 1 of acid, the reaction is represented by the equation:



If less sodium hydroxide is used, the two reactions occur together.

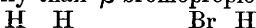
[With EUGEN KOWSKI.]—*α*-Bromopropionic acid yields both lactic and acrylic acids, behaving in the manner above stated. Barium

hydroxide has a somewhat different action from sodium hydroxide, giving other proportions of the two acids.

β -Bromopropionic acid yields hydracrylic and acrylic acids, the latter forming a larger proportion of the product than in the case of α -bromopropionic acid. The decomposition also takes place more rapidly. This fact is not in agreement with Wislicenus' theory as to the mechanism of the elimination of hydrogen haloids from organic



compounds. α -Bromopropionic acid, $\text{H} \cdot \dot{\text{C}} - \dot{\text{C}} - \text{H}$, should yield acrylic acid more easily than β -bromopropionic acid, which has either



the configuration $\text{H} \cdot \dot{\text{C}} - \dot{\text{C}} - \text{H}$ or $\text{H} \cdot \dot{\text{C}} - \dot{\text{C}} - \text{H}$; the first configura-

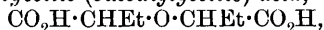


tion alone would yield acrylic acid, whilst the second would give ethylene, carbon dioxide, and sodium bromide.

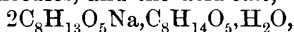
$\alpha\alpha$ -Dibromopropionic acid gives pyruvic and α -bromoacrylic acids and the so-called acryl-colloid; the velocity of the decomposition is affected by bases in the same way as with the foregoing substances. The proportion of α -bromoacrylic acid decreases with increasing dilution; it crystallises in readily volatile plates melting at 68° , and is decomposed by exposure to the air, or by treatment with sodium hydroxide, into acetylene. The acryl-colloid is formed only in acid solution; it consists of a jelly which, when dry, has the composition $\text{C}_{3n}\text{H}_{4n}\text{O}_{3n}$, and is completely insoluble in water, but soluble in alkali hydroxides. It is probably a polymeride of pyruvic acid, since ether extracts from the alkaline solution after acidification a syrup which combines with phenylhydrazine yielding the phenylhydrazone of pyruvic acid.

$\alpha\beta$ -Dibromopropionic acid decomposes more rapidly than the $\alpha\alpha$ -isomeride, yielding glyceric acid and α -bromohydracrylic acid, together with small quantities of pyruvic acid or, in acid solution, of acryl-colloid. According to Wislicenus' theory, the $\alpha\alpha$ - should decompose more rapidly than the $\alpha\beta$ -acid, since it can exist in only one configuration, namely, that which would yield bromohydracrylic acid.

[With HUGO SMELKUS.]—The main product of the decomposition of α -bromobutyric acid is hydroxybutyric acid, but both crotonic acid and *s*-diethyldiglycollic (*butodiglycollic*) acid,



are also formed. The latter is best prepared by dropping bromobutyric acid on to solid sodium hydroxide, mixing, and, after acidifying with dilute sulphuric acid, separating the oily layer, which consists mainly of crotonic acid, and then extracting the new acid with ether and purifying in the form of the barium salt. The acid crystallises at a low temperature and melts at 26° ; it boils at 117° under 11 mm. pressure. The normal *potassium* salt, $\text{C}_8\text{H}_{12}\text{O}_5\text{K}_2$, crystallises in hygroscopic needles, whilst the *potassium hydrogen* salt, $\text{C}_8\text{H}_{13}\text{O}_5\text{K}, \frac{1}{2}\text{H}_2\text{O}$, forms rectangular plates. The normal *sodium* salt, $\text{C}_8\text{H}_{12}\text{O}_5\text{Na}_2$, crystallises in leaflets or needles, and the acid salt,



forms needles. The *ammonium* salt crystallises in anhydrous needles, the *calcium* salt, $C_8H_{12}O_5Ca, H_2O$, forms microscopic prisms, the *barium* salt, $C_8H_{12}O_5Ba, \frac{1}{2}H_2O$, prisms, and the *copper* salt, $C_8H_{12}O_5Cu, H_2O$, pale blue needles; when anhydrous, the latter is deep azure blue. The *silver* salt, $C_8H_{12}O_5Ag_2$, crystallises in quadratic prisms, and the *lead* salt, $C_8H_{12}O_5Pb$, is amorphous.

s-Diethyldiglycollimide, $C_8H_{12}O_3 \cdot NH$, is prepared by dry distillation of the ammonium salt, and is a fusible solid distilling at $200-215^\circ$. *s-Diethyldiglycollic acid* can be distilled under diminished pressure, but at the ordinary pressure decomposes into carbon monoxide and propaldehyde and an acid which appears to be metameric with α -hydroxybutyric acid. When reduced with 50 per cent. hydriodic acid, *s-diethyldiglycollic acid* yields butyric acid and hydroxybutyric acid.

[With OSCAR GERLACH.]—When α -bromoisobutyric acid is decomposed by treatment with water at the ordinary temperature, a process which requires eighteen months, hydroxyisobutyric acid is alone produced, whereas by boiling with water 8 per cent. of methylacrylic acid is also formed; 14.8 per cent. of methylacrylic acid is formed when 1 mol. of $NNaOH$ is used at a temperature of 80° , and 75 per cent. when 4 mols. of 25 per cent. sodium hydroxide are employed.

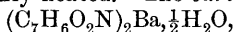
β -Bromoisobutyric acid yields only methylacrylic acid under all conditions. Wislicenus' theory indicates that the α -bromo-acid would yield methylacrylic acid rather than the β -bromo-acid.

Zinc methylacrylate, $(C_4H_5O_2)_2Zn$, crystallises in prisms and readily polymerises when heated. The *cadmium* salt forms small aggregates, the *strontium* salt needles, and the *lead* salt prisms or plates which polymerise on heating; the *copper* salt is a pale blue, insoluble precipitate.

[With FRITZ MORSCHÖCK and CARL DORNO.]—Bromomethylacrylic acid is formed when citradibromomethylsuccinic acid is boiled with three parts of water for four hours. Both bromo- and isobromo-methylacrylic acids are formed when a neutral solution of mesodibromomethylsuccinic acid is warmed at 60° , care being taken that the solution remains neutral. The bromo-acid separates first, whilst the isobromo-acid can be extracted with ether. *iso*Bromomethylacrylic acid crystallises in leaflets melting at 68° . Both acids decompose on heating into hydrogen bromide, carbon dioxide, and allene. When boiled for a short time, the isobromomethylacrylic acid is converted into bromomethylacrylic acid, but on prolonged boiling with aqueous sodium hydroxide both acids are decomposed, the *iso*-acid more slowly, into allylene. Heating of the calcium salts produces allene and allylene, the *iso*-acid being first transformed into bromomethylacrylic acid. This change is also effected by exposure of the chloroform solution, to which a trace of bromine has been added, to sunlight. The silver salts of both acids are decomposed on boiling with water, that of bromomethylacrylic acid yielding silver bromide, silver, carbon dioxide, and propaldehyde. The silver salt of the *iso*-acid changes more rapidly than the other according to the equation $C_4H_5O_2BrAg + H_2O = C_3H_6O + CO_2 + AgBr$. Permanganate oxidises both acids to acetic acid; a similar behaviour of the two acids is also observed when reduced or electrolysed.

[With CARL DORNO.]—Allene yields a compound with aqueous mercuric chloride, which has the composition $C_6H_8O_3Cl_6Hg_6$ and seems to be identical with the substance obtained from allylene by Kutscheroff (*Ber.*, 1884, 17, 13). In order to distinguish the two gases, dependence is especially to be placed on the fact that allylene precipitates ammoniacal silver and cuprous solutions, whilst allene does not. With alkaline mercury solutions, allylene gives a precipitate, $(C_3H_3)_2Hg$; allene does not. The tetrabromide of allylene is liquid and that of allene a solid melting at 0° . K. J. P. O.

Action of Cyanoacetic Acid on Crotonaldehyde. HUGO HAERDTL (*Monatsh.*, 1905, 26, 1391—1402. Compare Braun, *Abstr.*, 1896, i, 594; Doebner, *Abstr.*, 1900, i, 536).— α -Cyanosorbic acid, $CHMe:CH:CH:C(CN)\cdot CO_2H$, is formed by heating a molecular mixture of crotonaldehyde and cyanoacetic acid in an atmosphere of carbon dioxide, in a reflux apparatus, in a boiling water-bath for six hours. It crystallises from water in stout, yellow needles, 6—8 mm. long, softens and loses carbon dioxide at 150° , or melts and decomposes at 163° when quickly heated. The *barium* salt,

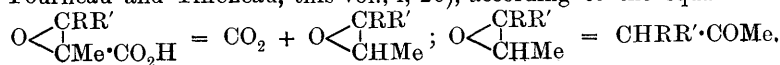


crystallises in nodular aggregates. With bromine in chloroform solution, the cyano-acid forms the *additive* compound, $C_7H_7O_2NBr_2$, which separates as a fine, white, crystalline powder and melts at 154 — 156° . When heated in small quantities at 150 — 160° until the evolution of carbon dioxide ceases, the cyano-acid forms *sorbonitrile*, $CHMe:CH:CH:CH\cdot CN$, which, when freshly distilled, is a clear, mobile liquid; it boils at 50 — 60° under 12 mm. pressure and gradually decomposes in a closed vessel with formation of a brown resin. When boiled with 10—12 per cent. aqueous potassium hydroxide in a reflux apparatus, the cyano-acid yields a brown, amorphous substance, $C_6H_8O_2(?)$, which is soluble in pyridine or glacial acetic acid, but is insoluble in aqueous sodium carbonate, and when boiled with aqueous baryta forms a *barium* salt, $(C_4H_5O_2)_2Ba$, whilst no definite product of hydrolysis could be obtained by heating the cyano-acid with alcoholic potassium hydroxide, dilute hydrochloric acid, or 40 per cent. sulphuric acid. G. Y.

General Method of Synthesising $\alpha\beta$ -Trisubstituted Glycidic Esters and Ketones. GEORGES DARZENS (*Compt. rend.*, 1905, 141, 766—768. Compare *Abstr.*, 1905, i, 116).—Ethyl α -chloropropionate readily condenses with ketones in the presence of sodium ethoxide to form the ethyl esters of the $\alpha\beta$ -trisubstituted glycidic

acids of the type $O\left\langle \begin{smallmatrix} CRR' \\ CMe\cdot CO_2Et \end{smallmatrix} \right.$ These are colourless liquids with

a faint odour, yielding on hydrolysis the corresponding acids, which are unstable and readily break down into carbon dioxide and the corresponding ketone, the latter being formed probably from an intermediate oxide by the migration of a hydrogen atom (compare Fourneau and Tiffeneau, this vol., i, 20), according to the equations:



In the following table are given the boiling points of the new ethyl trisubstituted glycidates and of the ketones prepared from them, together with the melting points of the semicarbazides of the latter.

Ketone.	Boiling point of corresponding ethyl glycidate.		Boiling point of ketone.		Melting point of semi- carbazide.
	Pressure.		Pressure.		
Acetone.....	80—82°	under 20 mm.	—	—	—
Methyl ethyl ketone ...	90—93	„ 22 „	—	—	—
Methyl <i>n</i> -propyl ketone	100—102	„ 16 „	—	—	—
Methyl <i>n</i> -hexyl „	152	„ 28 „	100—103°	under 26 mm.	86—87°
Methyl <i>n</i> -heptyl „	148—150	„ 16 „	101—103	„ 15 „	168—169
Methyl <i>n</i> -nonyl „	174—175	„ 15 „	132—135	„ 15 „	78—79
Acetophenone	151—154	„ 22 „	102—104	„ 20 „	172—173
<i>p</i> -Tolyl methyl ketone..	160—162	„ 19 „	116—118	„ 22 „	184—185

M. A. W.

Preparation of Pure Ethyl Alkylmalonates. ARTHUR MICHAEL (*J. pr. Chem.*, 1905, [ii], 72, 537—554. Compare Abstr., 1905, i, 564, 855).—On adding ethyl malonate to the equivalent amount of 50 per cent. aqueous potassium hydroxide, cooled to -10° , the mixture solidifies owing to the formation of ethyl potassiomalonate, which rapidly decomposes to ethyl potassium malonate and alcohol. This change takes place immediately when ethyl malonate is shaken with 1 per cent. aqueous potassium hydroxide.

The partial hydrolysis of ethyl ethylmalonate takes place in less than one minute with 1 per cent., in three minutes with 4 per cent., in thirty minutes with 12 per cent., and only to the extent of 20 per cent. in thirty minutes, with 25 per cent. aqueous potassium hydroxide. When shaken with 25 per cent. aqueous potassium hydroxide, a mixture of ethyl ethylmalonate and ethyl malonate develops heat, and if extracted with ether after one minute yields 86 per cent. of the ethyl ethylmalonate in a state of purity.

Ethyl diethylmalonate undergoes only slight hydrolysis when heated with 50 per cent. aqueous potassium hydroxide.

The propylmalonates resemble the ethylmalonates in their stability towards alkali hydroxides, whilst the methylmalonates undergo hydrolysis more easily, ethyl dimethylmalonate being hydrolysed rapidly with 50 per cent. aqueous potassium hydroxide.

These differences in behaviour are utilised in the detection of ethyl malonate and ethylmalonate, the presence of 1 and 2 per cent. of which, respectively, causes the formation of a white precipitate when ethyl diethylmalonate is shaken with 50 per cent. aqueous potassium hydroxide, and of ethyl diethylmalonate, small percentages of which appear as drops of oil, when ethyl ethylmalonate or malonate is shaken with dilute potassium hydroxide.

Application of these tests to the ethyl ethylmalonates obtained by the methods used by previous authors shows that these contain varying quantities of ethyl diethylmalonate which cannot be removed by fractional distillation or by Schey's method of purification (*Rec. Trav. chim.*, 1897, 16, 357).

To prepare pure ethyl ethylmalonate, the crude product is shaken with 25 per cent. aqueous potassium hydroxide and the resulting oil boiled with an excess of the same reagent in a reflux apparatus. After extracting the ethyl diethylmalonate with ether, the solution is again boiled with a further quantity of potassium hydroxide, neutralised with hydrochloric acid, and treated with calcium chloride. The calcium salt obtained in this manner yields pure ethyl ethylmalonate, which boils at 92° under 10 mm., or at 211° (corr.) under 748 mm. pressure, and has a sp. gr. 1.004 at 20°.

Ethyl diethylmalonate is purified by boiling with 50 per cent. aqueous potassium hydroxide; it boils at 228.5—229.5° (corr.).

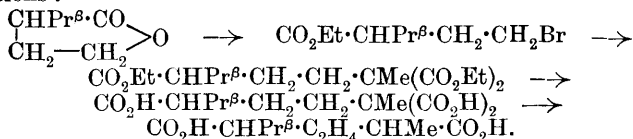
Ethyl methylmalonate, prepared by the action of methyl iodide on ethyl sodiomalonate and purified in the same manner as ethyl ethylmalonate, boils at 198.5—199° (corr.) under 765 mm. pressure. Ethyl dimethylmalonate, purified by shaking with a small quantity of 25 per cent. aqueous potassium hydroxide, boils at 196—196.5° (corr.) under 753 mm. pressure.

Ethyl propylmalonate boils at 225.5—226° (corr.) under 771 mm. pressure, and has a sp. gr. 0.9897 at 25°/25°. Ethyl dipropylmalonate boils at 248—249° (corr.).

Ethyl methylmalonate and ethylmalonate are obtained in yields of 90 and 70 per cent. of the ethyl malonate used when mixtures of ethyl malonate and methyl and ethyl iodide respectively are shaken with finely-divided potassium hydroxide. Ethyl dimethylmalonate is formed in the same manner from ethyl methylmalonate.

When shaken with ethyl iodide and powdered potassium hydroxide, ethyl acetoacetate forms ethyl ethylacetoacetate in a yield of 70—80 per cent. of its own weight, but in small yields in presence of water. The action of ethyl iodide and potassium hydroxide on ethyl ethylacetoacetate takes place only slowly and incompletely. G. Y.

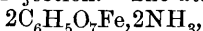
Synthesis of Dihydrocamphoric Acid. GUSTAVE BLANC (*Compt. rend.*, 1905, 141, 1030—1032).—The author has confirmed the constitution ascribed by Martine (Abstr., 1902, i, 629) to dihydrocamphoric acid, namely, α -methyl- δ -isopropyladipic acid (compare Perkin and Crossley, *Trans.*, 1898, 73, 23), by its synthesis from *iso*-propylsuccinic anhydride (Abstr., 1904, i, 369, 647; 1905, i, 631). *iso*-Propylsuccinic anhydride on reduction yields a mixture of α - and β -isopropylbutyrolactones, from which, on treatment with phosphorus pentabromide and subsequently with alcohol, a mixture of ethyl γ -bromo- α - and β -isopropylbutyrates is obtained, of which the α -isomeride condenses with ethyl sodiomethylmalonate to form a tricarboxylic ester. The corresponding free acid melts at 158°, losing carbon dioxide and forming α -methyl- δ -isopropyladipic acid, according to the equations:



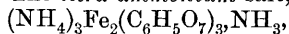
α -Methyl- δ -isopropyladipic acid has all the properties of dihydrocamphoric acid except that it is racemic; dihydrocamphoric acid, contrary to the statement of Perkin and Crossley, is optically active, having $[\alpha]_D^{20}$ $8^\circ 30'$ according to measurements made by Martine at the author's request. α -isoPropyladipic acid melting at 63° is obtained when ethyl sodiomalonate is substituted for ethyl sodiomethylmalonate in the above series of reactions. M. A. W.

Iron Citrates. GIUSEPPE SIBONI (*Chem. Centr.*, 1905, ii, 1623—1624; from *Boll. Chim. Farm.*, 44, 625—637).—Ferrous citrate, prepared by boiling a solution of citric acid with iron turnings for several days and concentrating in a vacuum, is sparingly soluble in water, but does not crystallise readily owing to the formation of the more soluble ferric citrate. If oxidation is prevented, the citrate separates out even in the presence of free citric acid (compare Martinotti and Cornelio, *Abstr.*, 1901, i, 667). Ferrous citrate is very readily soluble in ammonia, forming ferrous ammonium citrate (*loc. cit.*), which decomposes at 120° and is readily oxidised in solution, but is more stable in the presence of citric acid or an excess of acid ferrous citrate. Sodium ferrous citrate, prepared by neutralising crystalline ferrous citrate with sodium hydroxide, is more suitable for therapeutic application (compare Baroni, *Giorn. Farm. Chim.*, 53, 145).

Normal ferric citrate, $C_6H_5O_7Fe, 3H_2O$, is obtained by digesting freshly precipitated ferric hydroxide with citric acid for twenty-four hours at 60 — 65° , filtering, and evaporating the filtrate at 50 — 60° ; an anhydrous salt separates from the aqueous solution in the form of a red powder on the addition of ether. Ferric citrate has an acid reaction, and when treated with ammonia forms ammino- and ammonium salts. The monoammino-salt, $2C_6H_5O_7Fe, NH_3$, forms a slightly deliquescent, red powder, which has an acid reaction and is not suitable for subcutaneous injection. The diammino-salt,



prepared by the action of ammonia on an aqueous solution of the preceding salt or by the oxidation of ferrous ammonium citrate, is brown and more deliquescent than the monoammino-salt. The triammino-salt, $2C_6H_5O_7Fe, 3NH_3$, obtained by saturating a solution of ferric citrate with ammonia, is neutral and better adapted for subcutaneous injection. Ferric ammonium citrate, $H_2(NH_4)Fe_2(C_6H_5O_7)_2$, prepared by adding a solution of ammonia to a solution of ferric citrate, forms thin, yellowish-brown scales, is very deliquescent, and has a strong acid reaction. Ferric diammonium citrate, $H(NH_4)_2Fe_2(C_6H_5O_7)_3$, also obtained by the action of ammonia on a solution of ferric citrate, forms yellowish-green scales and is very deliquescent. Ferric triammonium citrate, $(NH_4)_3Fe_2(C_6H_5O_7)_3$, also separates in bright green scales and has an acid reaction. The tetra-ammonium salt,



prepared by neutralising a solution of ferric citrate with ammonia and evaporating at a low temperature, crystallises in scales. This salt is contained in the preparation described in the German Pharmacopœia; the preparations of the Russian and Norwegian Pharmacopœias should contain 9.21 and 17.33 per cent. of iron respectively. E. W. W.

Laboratory Notes. [*Diisobutyl Ketone. isoNitrosobenzylacetone. isoButyryl- and isoValeryl-phenylhydrazines. Erucic Acid.*] GIACOMO PONZIO (*Gazzetta*, 1905, **35**, ii, 394—398).—*Diisobutyl ketone* (valerone), $\text{CO}(\text{CH}_2\cdot\text{CHMe}_2)_2$, prepared by the action of zinc *isobutyl* on *isovaleryl chloride*, boils at $164\text{--}166^\circ$ under 741 mm. pressure and gives a *semicarbazone*, $\text{C}_{10}\text{H}_{21}\text{ON}_3$, crystallising from light petroleum in white plates melting at 115° (compare Schmidt, *Ber.*, 1872, **5**, 600; Williams, *Trans.*, 1879, **35**, 130).

isoNitrosobenzylacetone can be obtained readily and in good yield by adding *isoamyl nitrite* and *benzylacetone* to alcoholic sodium ethoxide and subsequently washing the alkaline solution with ether and saturating it with carbon dioxide. It crystallises from light petroleum in long, shining needles melting at $80\text{--}81^\circ$ (compare Ceresole, *Abstr.*, 1883, 41).

With phenylhydrazine, *isobutyryldinitroethane* yields *isobutyryl-phenylhydrazine*, whilst *isovaleryldinitroethane* gives *isovalerylphenylhydrazine*, *aa-dinitroethane* being formed in both cases.

On passing dry hydrogen bromide into a cold acetic acid solution of erucic acid, the latter is converted partly into the isomeric planosymmetric brassidic acid and partly into *bromobehenic acid*, $\text{C}_{22}\text{H}_{43}\text{O}_2\text{Br}$, which crystallises from alcohol in white prisms melting at $39\text{--}40^\circ$.

T. H. P.

Digitoxose. HEINRICH KILIANI (*Ber.*, 1905, **38**, 4040—4043. Compare *Abstr.*, 1899, i, 932).—Digitoxose is considered now to have the constitution $\text{OH}\cdot\text{CHMe}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CHO}$. It is an aldehyde, as, on oxidation with bromine in aqueous solution and removal of the hydrogen bromide which is formed by means of silver oxide, it yields a solution containing the *lactone* of digitoxonic acid; this, when boiled with calcium carbonate, forms *calcium digitoxonate*, $(\text{C}_6\text{H}_{11}\text{O}_5)_2\text{Ca}$, which is precipitated as a glutinous mass.

As digitoxosecarboxylic acid also forms a lactone, two of the hydroxyl groups of digitoxose must be in the β - and γ -positions, whilst the δ -position of the third hydroxyl is shown by the conversion of calcium digitoxonate into *$\alpha\beta$ -dihydroxyglutaric acid* when it is oxidised with concentrated nitric acid under cooling with ice, and finally at $35\text{--}37^\circ$. The acid is isolated in the form of its *calcium salt*, $\text{C}_5\text{H}_6\text{O}_6\text{Ca}$, which is precipitated from its aqueous solution by means of alcohol, and on liberation from this, as its *lactone*, $\text{C}_5\text{H}_6\text{O}_5$. This is obtained as an oil, which, after some time, solidifies when stirred; it commences to soften at about 115° , melts at 120° , and differs from the previously known dihydroxyglutaric acids in that after cooling and resolidification it melts sharply at 120° (compare Kiliani and Herold, *Abstr.*, 1905, i, 739; Kiliani and Loeffler, *ibid.*, 858); it is slightly dextrorotatory in 7.8 per cent. solution in a 2 dm. tube.

G. Y.

Mineral Compounds which may possess the Rôle, like Diastase, of Liquefying Malt. JULES WOLFF (*Compt. rend.*, 1905, **141**, 1046—1048).—Starch (25 grams) was treated with 50 c.c. of a solution containing 0.1 per cent. of potassium permanganate and

10—15 per cent. of sulphuric acid (or 6—7 per cent. of hydrochloric acid) for $1\frac{1}{2}$ to 2 hours, washed with distilled water, and dried at 30° . The starch underwent no appreciable change in appearance or weight, and when treated with malt or acids yielded the same products as ordinary starch. When, however, a small amount of a basic substance (ammonia, alkaline oxides, &c.) is present and the temperature is raised to 70° , it liquefies immediately. Acids, neutral salts, and acid phosphates have no action.

When the starch, treated as described, is mixed with distilled water, the liquid is slightly acid (to phenolphthalein). The liquefaction does not, however, occur exactly at the point when the acid is just neutralised, but may take place both in slightly acid and in slightly alkaline conditions.

The change produced in the starch is not due to the removal of mineral salts.

N. H. J. M.

Liquefying and Saccharifying Actions on Starch. PAUL PETIT (*Compt. rend.*, 1905, 141, 1247—1249. Compare preceding abstract).—Infusions of malt behave like guaiacol towards ferrous, ferric, manganous, and manganic compounds. Ferric and manganic compounds of malt infusion are reduced by hydrogen. A known volume of sodium hydroxide solution is added to the infusion containing the aluminium compound in an atmosphere of hydrogen. The soda is then exactly neutralised with acetic acid and tincture of guaiacol added. No coloration is produced; addition of a drop of hydrogen peroxide at once produces a strong blue colour.

A solution of commercial albumin (0.25 per cent.) was shaken with a mixture of equal parts of ferrous, ferric, and manganous oxides and filtered. The solution, which after a time became turbid, was again filtered. The clear liquid shows the same reaction with tincture of guaiacol as malt infusion, and it also liquefies starch, the action being accelerated by addition of asparagine. In presence of asparagine, there is also a slight saccharification.

N. H. J. M.

Starch, Glycogen, and Cellulose. ZDENKO H. SKRAUP [and, in part, E. GEINSPERGER, E. VON KNAFFL-LENZ, FRANZ MENTER, and H. SÍRK] (*Monatsh.*, 1905, 26, 1415—1472).—Soluble starch was suspended in eight times its weight of acetic anhydride saturated with hydrogen chloride at -20° ; after fourteen days at the laboratory temperature, the chief product was chlorononadeca-acetylerythrodextrin; after two months, an amorphous substance, having the composition of acetyl-chloromaltose; and after four months, tetra-acetylchlorodextrose.

Chlorononadeca-acetylerythrodextrin, $(C_6H_7O_5)_6ClAc_{19}$, is soluble in benzene, but insoluble in light petroleum, has $[\alpha]_D + 186.20^{\circ}$, and when treated with silver acetate in glacial acetic acid solution yields the icosa-acetyl derivative, $(C_6H_7O_5)_5(C_6H_7O_6)Ac_{20}$, which sinters at 110° and has $[\alpha]_D + 145.3^{\circ}$. When hydrolysed by means of 2*N* alcoholic potassium hydroxide, under cooling with snow, it yields erythrodextrin, having $[\alpha]_D + 160.8^{\circ}$. The product obtained on shaking soluble starch with acetic anhydride, saturated with hydrogen chloride at 0° . for seven hours in a sealed tube at 40° is a mixture of

acetylchloro-derivatives of the starch and its decomposition products. When purified by precipitation from its benzene solution by light petroleum and by ether, the *acetylchloro*-derivative of soluble starch contains 0.268 per cent. of chlorine, from which its molecular weight is calculated as 13230. It sinters at 170°, becomes brown at 240–250°, decomposes with evolution of a gas at 270°, does not give a coloration with iodine, and when hydrolysed with 2*N* alcoholic potassium hydroxide yields soluble starch. The minimum formula for soluble starch must be, therefore, $(C_6H_{10}O_5)_{46-50}$. When heated on the water-bath with silver acetate in glacial acetic acid solution, the acetylchloro-derivative of soluble starch yields Pregl's triacetyl-soluble starch (Abstr., 1902, i, 136) and a *substance* which has $[\alpha]_D 151^\circ$, and must contain acetyl derivatives of the decomposition products of soluble starch, as on hydrolysis it yields a substance which gives a violet coloration with iodine.

The action of acetic anhydride saturated with hydrogen chloride at -12° on glycogen at the laboratory temperature for twenty hours leads to the formation of an *acetylchloro*-compound, which contains 0.15 per cent. of chlorine and has the molecular weight, calculated 23630, observed about 25000. It is a white, amorphous substance, is readily soluble in benzene, chloroform, glacial acetic acid, ethyl acetate, or acetone, and when shaken with silver acetate in glacial acetic acid solution forms the *triacetyl* derivative, $(C_6H_7O_5Ac_3)_x$, which sinters at 165°, becomes opaque at 180°, and melts at 240°. It has $[\alpha]_D +132.34^\circ$, and on hydrolysis yields a substance, $(C_6H_{10}O_5)_{100}$, which has $[\alpha]_D 192.1^\circ$, and is more soluble than glycogen, which has $[\alpha]_D 196.6^\circ$.

The action of acetic anhydride saturated with hydrogen chloride at -15° on cellulose (*a*) for forty-eight hours leads to the formation of a brown, amorphous *derivative*, $(C_6H_7O_2)_{34}(OAc)_{101}Cl$, which on hydrolysis with alcoholic potassium hydroxide yields cellulose, $(C_6H_{10}O_5)_{34}$, (*b*) or for fourteen days, leads to the formation of hepta-acetylchlorocellobiose, which melts at 195° and has $[\alpha]_D +75.21^\circ$. Hepta-acetylchlorocellobiose, prepared from cellobiose acetate (Skraup and König, Abstr., 1902, i, 35), melts at 195° and has $[\alpha]_D +74.87^\circ$. When warmed with silver acetate and glacial acetic acid, it yields an *acetate*, which melts at 200°, has $[\alpha]_D -30.05^\circ$, and is not identical with cellobiose acetate, which melts at 228° and has $[\alpha]_D +43.64^\circ$. On hydrolysis with alcoholic potassium hydroxide, the acetate melting at 200° yields a brown mass, which does not deposit cellobiose on solution in water and addition of a crystal of that substance. G. Y.

Decomposition of Nitrocellulose at Temperatures below that of Ignition. ALEXIS V. SAPOSCHNIKOFF and W. JAGELLOWITSCH (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 822–828. Compare Abstr., 1904, i, 799).—The authors have determined the velocities of decomposition, at different temperatures below that of ignition, of ordinary pyroxylin having the composition $C_{24}H_{29}(NO_3)_{11}O_9$ by measuring the volumes of gas evolved in definite time intervals. The volume-time curves for temperatures from 120° to 135° are widely different in character from those obtained at 140–150°, but both exhibit points of

inflexion corresponding with maximal values of dv/dt (v = volume of gas and t = time) ; the relation between these maximal velocities and the temperature is expressed by the following equations : (1) between 120° and 135° , $(dv/dt)_{\max.} = -2.22 + 0.0192T$; (2) between 135° and 150° , $(dv/dt)_{\max.} = -64.22 + 0.48T$. At 150° , the decomposition of the pyroxylin is represented by the equation : $C_{24}H_{29}(NO_3)_{11}O_9 = 6.27CO_2 + 3.58CO + 5.37NO + 2.71N_2 + 8H_2O + C_{14.15}H_{13}O_{12.5}N_{0.21}$, and at 120° the products are

$2.31CO_2 + 1.75CO + 2.06NO + 2.7N_2 + 14.41H_2O + C_{19.94}H_{0.2}O_{19.16}N_{3.56}$. At temperatures above 135° , the solid residue contains practically no nitrogen, whilst at lower temperatures about 25—30 per cent. of the nitrogen, but very little hydrogen, remains in the undecomposed matter.

T. H. P.

Behaviour of Vegetable and Animal Textile Fibres with Solutions of Metallic Salts. W. SCHELLENS (*Arch. Pharm.*, 1905, 243, 617—627).—One gram of the fibre was allowed to remain for several days in 50 c.c. of the solution of the metallic salt. The total amount of salt taken up was in part merely adsorbed by the fibre ; this was removed by washing and boiling with water until the wash-water no longer gave any reaction of either constituent of the salt ; the amount then remaining “fixed” in the fibre was determined if possible (compare Zacharias, *Abstr.*, 1902, i, 725). The amounts are expressed as percentages of the weight of the fibre. As a rule, it is either the base or the acid of the salt that is taken up ; proportionately more is taken up out of dilute solutions as compared with strong ones, and the amount taken up is greater as the extent to which the salt is hydrolysed is greater ; in no case was a coloration of the fibre observed.

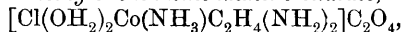
With ferric chloride, the following results were obtained, in which the numbers refer to the weight of iron fixed from solutions containing 1 and 0.1 per cent. of iron respectively : cotton-wool, 0.112, 0.112 ; filter-paper, 0.23, 0.123 ; precipitated cellulose, 0.112, 0.112 ; woolly fibre from the seeds of *Eriodendron anfractuosum*, 1.01, 0.56 ; jute, 0.56, 0.44 ; raw silk, 0.67, 0.67 ; yellow Japanese silk (organsin), 0.67, 0.615 ; precipitated silk, 0.24 ; wool, 0.84, 0.36. From alcoholic ferric chloride and from aqueous ferric acetate, more iron is fixed, corresponding with the greater hydrolysis (Schaer, *Abstr.*, 1901, ii, 603). The case of wool and ferric acetate is exceptional, however, less iron being fixed than from aqueous ferric chloride of equivalent strength. Mercury is taken up by the fibres from aqueous mercuric chloride, and also from aqueous mercuric cyanide to a smaller extent ; only a small portion is fixed, however. From aqueous mercuric acetate, large quantities of mercury are taken up, amounting to 12.3 in the case of wool. Lead is also taken up from the aqueous nitrate ; some of it is fixed in the case of *Eriodendron*, silk, and wool, none in the case of cotton-wool and paper. Chromium trioxide is taken up from aqueous potassium dichromate, and iodine (iodide?) from aqueous potassium iodide. Potassium nitrate in aqueous solution is reduced to nitrite or even further ; in the case of silk and wool in a 0.01 per cent.

solution, neither nitrate nor nitrite could be detected after eight days, and in the first case the solution had become alkaline, not so in the other.

C. F. B.

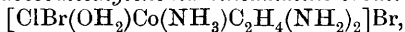
Mixed Triamine Cobalt Salts containing Ethylenediamine and Ammonia. ALFRED WERNER and AD. GRÜN (*Ber.*, 1905, **38**, 4033—4040. Compare Werner, *Zeit. anorg. Chem.*, 1895, **8**, 174; Jörgensen, *Abstr.*, 1897, ii, 41, 453).—*Trinitrocobaltethylenediamineammine*, $(\text{NO}_2)_3\text{Co}(\text{NH}_3)\text{C}_2\text{H}_4(\text{NH}_2)_2$, is prepared by adding ethylenediamine to a solution of Erdmann's sodium tetranitrodiammincobalt at 60° ; it crystallises in brown leaflets or long, broad, feathery needles, is stable towards cold hydrochloric acid, but when warmed with the acid is converted into *dichloroaquocobaltethylenediamineammine chloride*, $[\text{Cl}_2(\text{OH}_2)\text{Co}(\text{NH}_3)\text{C}_2\text{H}_4(\text{NH}_2)_2]\text{Cl}$, which crystallises in small, greenish-black, slightly dichroic needles, dissolves in ice-cold water to form a green solution which becomes blue, and on dilution red; silver nitrate precipitates the total chlorine from the aqueous solution as silver chloride. When heated, the neutral, aqueous solution deposits cobalt hydroxide; hot hydrochloric acid decomposes the chloride with formation of "ethylenediamine chlorocobaltoate," which separates in blue leaflets. The action of sodium nitrite on the chloride leads to the formation of trinitrocobaltethylenediamineammine. The *nitrate*, $[\text{Cl}_2(\text{OH}_2)\text{Co}(\text{NH}_3)\text{C}_2\text{H}_4(\text{NH}_2)_2]\text{NO}_3$, is formed by treating the chloride with nitric acid of sp. gr. 1.4; it crystallises in green scales having a metallic lustre and is extremely soluble in water.

Chlorodiaquocobaltethylenediamineammine oxalate,

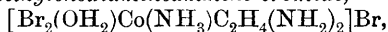


is formed by heating the chloride of the dichloroaquo-compound with oxalic acid in aqueous alcoholic solution; it crystallises in glistening, blue leaflets, is moderately soluble in hot water, when treated with hydrochloric acid in aqueous solution yields the dichloroaquochloride from which it is formed, and gives a precipitate of calcium oxalate with calcium chloride in ammoniacal solution. It forms silver chloride only slowly with silver nitrate in aqueous solution, and when heated at 105° loses H_2O .

Chlorobromoaquocobaltethylenediamineammine bromide,



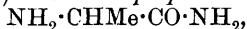
formed by the action of hydrobromic acid of sp. gr. 1.49 on the dichloroaquochloride, crystallises in small, olive-green needles, sinters and loses H_2O at 105° , forming a yellow crust which dissolves in water to form a yellow solution, and forms a sparingly soluble *iodide* with aqueous potassium iodide and an easily soluble, light green *nitrate* with concentrated nitric acid. When warmed with water and treated with an equal volume of hydrobromic acid of sp. gr. 1.49, it forms *dibromoaquocobaltethylenediamineammine bromide*,



which crystallises in small, stellate aggregates of needles, showing strong dichroism from bluish-black to brown, forms a green powder when finely divided, and dissolves in water to a brown solution.

G. Y.

Amides of α - and β -Aminopropionic Acids. ANTOINE P. N. FRANCHIMONT and H. FRIEDMANN (*Proc. R. Akad. Wetensch. Amsterdam*, 1905, 8, 475—477).— α -Aminopropionamide,



crystallises from alcohol in needles, is very soluble and hygroscopic and melts at 62° ; it gives a crystalline *hydrochloride*, a crystalline, orange-red *platinichloride*, and a yellow *picrate* melting at 199° .

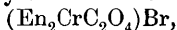
β -Aminopropionamide, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$, is very hygroscopic and soluble, but was purified by precipitating the methyl-alcoholic solution with ether and forms beautiful crystals melting at 41° .

Neither compound is identical with the supposed aminopropionamide isolated from urine by Baumstark in 1873. T. M. L.

Configuration of Stereoisomeric Chromium Salts. PAUL PFEIFFER [with A. TRIESCHMANN] (*Annalen*, 1905, 342, 283—305. Compare Abstr., 1905, i, 33).—It was shown (*loc. cit.*) that two series of isomeric chromium compounds could be obtained and converted into two corresponding series of stereoisomeric oxalates by treatment with potassium oxalate. Thus, violet dichlorodiethylenediaminechromium chloride yields red crystals of an oxalate, $\text{Cr}_2(\text{C}_2\text{O}_4)_3, 3\text{En}$, where En = ethylenediamine. The isomeric green salt, on the other hand, gives a violet compound, $\text{Cr}_2\text{Cl}_2(\text{C}_2\text{O}_4)_2, 3\text{En}$.

A constitution for the red salt, $\text{Cr}_2(\text{C}_2\text{O}_4)_3, 3\text{En}$, may be obtained by considering it as formed from any two of the complex ions, $(\text{En}_3\text{Cr})'''$, $(\text{En}_2\text{CrC}_2\text{O}_4)'$, $[\text{EnCr}(\text{C}_2\text{O}_4)_2]'$, or $[\text{Cr}(\text{C}_2\text{O}_4)_3]'''$; four formulæ are possible, $(\text{En}_3\text{Cr})[\text{Cr}(\text{C}_2\text{O}_4)_3]$, $(\text{En}_2\text{CrC}_2\text{O}_4)[\text{EnCr}(\text{C}_2\text{O}_4)_2]$, and two formulæ which imply a double molecular weight, $(\text{En}_3\text{Cr})[\text{EnCr}(\text{C}_2\text{O}_4)_2]_3$, and $(\text{En}_2\text{CrC}_2\text{O}_4)_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$.

Since, however, the red salt reacts with concentrated hydrobromic acid yielding the oxalodiethylenediaminechromium bromide,

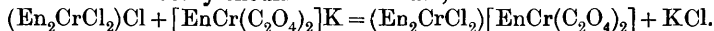


identical with the salt described by Werner and Schwarz, the formulæ $(\text{En}_2\text{CrC}_2\text{O}_4)[\text{EnCr}(\text{C}_2\text{O}_4)_2]$ and $(\text{En}_2\text{CrC}_2\text{O}_4)_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ are alone possible. If the red salt is treated with potassium iodide, the insoluble oxalodiethylenediaminechromium iodide, $(\text{En}_2\text{CrC}_2\text{O}_4)\text{I}$, separates, whilst the soluble potassium dioxaloethylenediaminechromate, $[\text{EnCr}(\text{C}_2\text{O}_4)_2]\text{K}$, remains in solution, and, on adding excess of potassium iodide solution, is thrown down as the *double salt*, $[\text{EnCr}(\text{C}_2\text{O}_4)_2]\text{K}, \text{KI}, 2\text{H}_2\text{O}$. These facts are in favour of the formula $(\text{En}_2\text{CrC}_2\text{O}_4)[\text{EnCr}(\text{C}_2\text{O}_4)_2]$ for the red salt.

The red salt was then synthesised from the oxalodiethylenediaminechromium bromide, $(\text{En}_2\text{CrC}_2\text{O}_4)\text{Br}$, and the potassium salt, $[\text{EnCr}(\text{C}_2\text{O}_4)_2]\text{K}$, which were mixed in concentrated aqueous solution; the red salt must therefore be called *oxalodiethylenediaminechromium dioxaloethylenediaminechromate*.

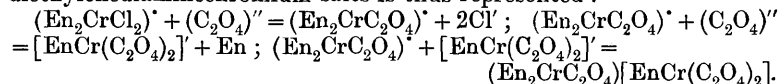
The isomeric salt, $(\text{En}_3\text{Cr})[\text{Cr}(\text{C}_2\text{O}_4)_3]$, was obtained from triethylenediaminechromium chloride, $(\text{En}_3\text{Cr})\text{Cl}_3$, and potassium oxalochromate, $[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{K}_3$; it crystallised in green, lustrous leaflets with 6 or $7\text{H}_2\text{O}$, and was decomposed by a concentrated solution of potassium iodide into the iodide, $(\text{En}_3\text{Cr})\text{I}_3$, and the oxalochromate, $[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{K}_3$.

The violet salt, $\text{Cr}_2\text{Cl}_2(\text{C}_2\text{O}_4)_2 \cdot 3\text{En}$, has an analogous constitution, $(\text{En}_2\text{CrCl}_2)[\text{EnCr}(\text{C}_2\text{O}_4)_2]$, and is *dichlorodiethylenediaminechromium dioxaloethylenediaminechromate*. With concentrated nitric acid, it yielded the green nitrate, $(\text{En}_2\text{CrCl}_2)\text{NO}_3$, and it can be synthesised from dichlorodiethylenediaminechromium chloride and potassium dioxaloethylenediaminechromate,

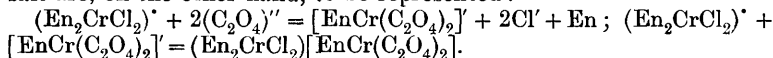


Further, the analogous violet *cobalt* salt, $(\text{En}_2\text{CoCl}_2)[\text{EnCr}(\text{C}_2\text{O}_4)_2]$, was prepared and crystallised in leaflets.

The reactions between potassium oxalate and the violet dichlorodiethylenediaminechromium salts is thus represented :



The reactions between potassium oxalate and the green dichloro-salt are, on the other hand, to be represented :



In the case of both salts, the oxalo-group replaces the chlorine of the positive ion, En_2CrCl_2 , in the green salt, converting it into the negative dioxalo-ion, $\text{EnCr}(\text{C}_2\text{O}_4)_2$, but in the case of the violet salt also giving the mono-oxalo-positive ion, $\text{En}_2\text{CrC}_2\text{O}_4$.

It is pointed out that all these observations are in agreement with the view that the two series of salts are stereoisomeric. K. J. P. O.

Resolution of Leucine into its Optically Active Components by means of its Formyl Derivative. EMIL FISCHER and OTTO WARBURG (*Ber.*, 1905, 38, 3997—4005. Compare Abstr., 1900, i, 646).—*Formyl-leucine*, $\text{C}_7\text{H}_{13}\text{O}_3\text{N}$, prepared by heating leucine repeatedly with 98.5 per cent. formic acid and washing carefully so as to remove unchanged leucine, softens at about 112° and melts at 115 — 116° (corr.); it crystallises from water in microscopic octahedra, and is converted by phosphorus pentachloride into a *formyl-leucyl chloride*, $\text{C}_4\text{H}_9\text{CH}(\text{NH}\cdot\text{CHO})\cdot\text{COCl}$, which is a colourless, indistinctly crystalline powder.

Formylglycine, $\text{CHO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, prepared by the action of formic acid on aminoacetic acid, crystallises from water or alcohol, softens at 149° , and melts and decomposes at 153 — 154° (corr.).

When formyl-leucine is heated with an alcoholic solution of brucine, the *brucine* salt of formyl-*d*-leucine separates in a nearly pure state, and, on decomposing the latter with *N*-sodium hydroxide, *formyl-d-leucine* is obtained; it crystallises from water in long, thin prisms, melts at 141 — 144° (corr.) and has $[\alpha]_D + 18.8^\circ$ at 20° in 10 per cent. alcoholic solution. *Formyl-l-leucine*, prepared by decomposing the more soluble brucine salt, has the same melting point as the *d*-form and $[\alpha]_D - 18.5^\circ$ at 20° .

To hydrolyse the formyl-derivatives, they are heated with 10 per cent. hydrochloric acid, the excess of hydrochloric acid and the formic acid removed by distilling under reduced pressure, and the active amino-

acid separated by adding the calculated quantity of lithium hydroxide in alcoholic solution. *d*-Leucine has $[\alpha]_D - 15.6^\circ$ at 20° , whilst *l*-leucine has $[\alpha]_D + 15.6^\circ$ at the same temperature. These values agree fairly closely with those obtained with the active leucines prepared from the benzoyl-leucines (Fischer, *loc. cit.*), but a specimen of *l*-leucine prepared from proteids by E. Schulze had $[\alpha]_D + 16.9^\circ$. On the other hand, *d*-leucine obtained from the urine of a rabbit to which inactive leucine had been administered had $[\alpha]_D - 15.5^\circ$ at 20° . If the value obtained with Schulze's product corresponds with the true active leucine, the products prepared from the formyl and benzoyl derivatives must contain about 10 per cent. of the racemic form. W. A. D.

Synthesis of Polypeptides. X. Polypeptides of the Diamino- and Hydroxyamino-acids. EMIL FISCHER and UMETARO SUZUKI (*Ber.*, 1905, 38, 4173—4196. Compare Abstr., 1905, i, 121).—*Diamino-propionic acid dipeptide* is obtained as a tough, gummy mass with an alkaline reaction on heating the hydrochloride of the dimethyl ester with water at 80° ; the *picrate* is a citron-yellow, crystalline powder, which sinters at 200° and melts and decomposes at 222° (corr.); the crystalline *hydrochloride* decomposes above 250° . Inactive *lysyl-lysine*, $C_{12}H_{26}O_3N_4$, forms a yellow, crystalline *picrate* which sinters at 170° , melts at 185° (corr.) to a bright brownish-red oil, and decomposes on further heating; the *hydrochloride* crystallises in short, twin prisms melting at about 205° (corr.). Histidine anhydride forms a *picrate* separating in stellar aggregates of citron-yellow, flat crystals, which when heated become brown at 235° (corr.) and decompose at 255° (corr.); the *hydrochloride* crystallises in thin, colourless prisms aggregated in star-like clusters, which melt and decompose at about 320° (corr.).

Histidylhistidine, $C_{12}H_{16}O_3N_6$, forms a *picrate* crystallising in citron-yellow prisms which melt at 165 — 175° .

Arginine methyl ester forms a citron-yellow, crystalline *picrate*, which becomes brown at 200° and melts and decomposes at about 218° (corr.), and a *nitrate* crystallising in large prisms and melting at 189° (corr.).

isoSerylisoserine methyl ester, $C_7H_{14}O_5N_2$, forms large crystals which begin to change at 100° and are completely melted at 180° .

isoSerylisoserine is a colourless powder which sinters at 220° and decomposes at a higher temperature; its aqueous solution has an acid reaction.

Serine methyl ester is a colourless, strongly alkaline syrup; the *hydrochloride* forms colourless, transparent, hexagonal plates melting at about 114° (corr.) and decomposing above this temperature. *Serine anhydride*, $C_6H_{10}O_4N_2$, is obtained either as microscopic, four-sided, oblique plates, which become brown at 265° (corr.) and decompose at 280° (corr.), or in long, narrow, pointed prisms melting at 226° (corr.).

Serylserine is obtained as a mixture of two isomerides; the one present in greater quantity crystallises in stellate leaflets and on heating becomes brown at 200° and decomposes at 210° (corr.). The aqueous solution is strongly acid and dissolves copper oxide to form a blue

solution. The *hydrochloride* of the *ester* crystallises in star-like aggregates of pointed needles.

A method of preparing arginine from edestin is described.

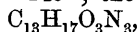
E. F. A.

Action of Carbamide on Compounds of Cyanoacetic Acid.

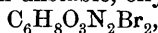
GUSTAV FRERICHs and L. HARTWIG (*J. pr. Chem.*, 1905, [ii], 72, 489—510).—When boiled together, carbamide and ethyl cyanoacetate

interact to form an ester, $\text{CO} \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, which crystallises from water in long, colourless needles, melts and decomposes at 162° , has the solubility 1:8333 in water at 24° , and gives a blood-red coloration with traces of aqueous ferric chloride. It has acidic properties, liberates carbonic and acetic acids from their salts, and in hot aqueous solution dissolves metallic zinc with evolution of hydrogen. The *potassium*, $\text{C}_6\text{H}_7\text{O}_3\text{N}_2\text{K} \cdot 2\text{H}_2\text{O}$, *ammonium*,

silver, and *copper*, $(\text{C}_6\text{H}_7\text{O}_3\text{N}_2)_2\text{Cu} \cdot 2\text{H}_2\text{O}$, derivatives are described; the *aniline* compound, $\text{C}_6\text{H}_8\text{O}_3\text{N}_2 \cdot \text{C}_6\text{H}_7\text{N}$, crystallises in needles and melts and decomposes at $144\text{--}145^\circ$; the *m-toluidine* compound,

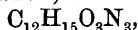


crystallises in white leaflets and melts and decomposes at 143° ; the *strychnine* compound, $\text{C}_6\text{H}_8\text{O}_3\text{N}_2 \cdot \text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2$, crystallises in sheaves of flat needles and melts and decomposes at 188° . The ester does not interact with benzaldehyde, formaldehyde, or hydroxylamine; on hydrolysis with alcoholic potassium hydroxide or aqueous ammonia, it yields carbon dioxide, alcohol, ammonia, and acetic acid; when heated with 25 per cent. hydrochloric acid in a reflux apparatus, it yields pure ammonium chloride, but when warmed with dilute nitric acid, a mixture of ammonium nitrate and oxalate. With bromine in aqueous solution, it forms an unstable, oily *additive* compound,



which is soluble in ether and liberates iodine from potassium iodide.

The corresponding *methyl ester*, $\text{CO} \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$, is formed by heating carbamide with methyl cyanoacetate; it crystallises from water in colourless leaflets containing $1\frac{1}{2}\text{H}_2\text{O}$, melts at 116° , or when anhydrous at 128° , gives a red coloration with aqueous ferric chloride, and is slightly more soluble than the ethyl ester, which it resembles in its chemical properties. The *potassium*, $\text{C}_5\text{H}_5\text{O}_3\text{N}_2\text{K}$, *ammonium*, $\text{C}_5\text{H}_5\text{O}_3\text{N}_2\text{NH}_4$, and *copper*, $(\text{C}_5\text{H}_5\text{O}_3\text{N}_2)_2\text{Cu} \cdot \frac{1}{2}\text{H}_2\text{O}$, derivatives are described; the *aniline* compound, $\text{C}_5\text{H}_6\text{O}_3\text{N}_2 \cdot \text{C}_6\text{H}_7\text{N}$, crystallises in white leaflets and melts at 120° ; the *m-toluidine* compound,



forms sheaves of slender needles and melts and decomposes at $120\text{--}121^\circ$; the *strychnine* compound, $\text{C}_{26}\text{H}_{28}\text{O}_5\text{N}_4$, crystallises in flat, white needles and melts and decomposes at 211° . The methyl ester forms an unstable bromine derivative similar to that obtained from the ethyl ester.

G. Y.

Mercuric Oxycyanide. KARL HOLDERMANN (*Arch. Pharm.*, 1905, 243, 600—617. Compare Holdermann, *Abstr.*, 1904, i, 301, and Richard, *J. Pharm. Chim.*, 1903, 18, 553).—By dissolving mercuric oxide in aqueous mercuric cyanide and crystallising the solution fractionally, it was shown that only one oxycyanide is formed; this has the composition $\text{Hg}(\text{CN})_2, \text{HgO}$. It is never possible to convert mercuric cyanide quantitatively into this compound; the most convenient method of separation is to mix the cyanide and oxide in equivalent proportions and moisten the mixture with a little water in a conical flask; heat the mixture for four hours on the water-bath, replacing the water as it evaporates; extract the mass with boiling water (500 c.c. for 13.5 grams of cyanide and 11.5 grams of oxide); filter the solution, and allow it to crystallise; in these circumstances, about 80 per cent. of the cyanide is obtained as oxycyanide.

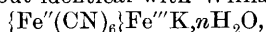
The amount of oxide in a sample of mercuric oxycyanide can be determined very readily and accurately by adding sodium chloride to a solution of the sample and titrating the oxide with *N*/10 hydrochloric acid with methyl-orange as indicator. Commercial oxycyanide contains but a small proportion of oxide.

The pure oxycyanide in aqueous solution gives no yellow coloration with potassium iodide, but an almost colourless, crystalline precipitate which dissolves in excess of the aqueous potassium iodide forming a colourless solution. Its electrolytic conductivity is even less than that of mercuric cyanide. The antiseptic action ascribed to it has been observed with very impure samples, and may not belong to the pure substance at all.

Methods of analysing samples of mercuric oxycyanide and tabloids containing it and sodium hydrogen carbonate are described in detail.

C. F. B.

Blue Iron-cyanogen Compounds and the Cause of their Colour. III. KARL A. HOFMANN and F. RESENSCHECK (*Annalen*, 1905, 342, 364—374. Compare *Abstr.*, 1905, i, 756).—It has been shown (*loc. cit.*) that the blue iron-cyano-compounds, formed either from ferric salts and ferrocyanides or ferrous salts and ferricyanides, are to be regarded as derivatives of potassium ferrocyanide in which potassium is either wholly or partly replaced by trivalent iron. The substances obtained on oxidising the compounds formed from ferrous salts and ferrocyanides do not belong to this class. The material so prepared from potassium ferrocyanide and a ferrous salt in molecular proportions in acid solution is quite different from the soluble Prussian blue, but identical with Williamson's violet,



which is produced on oxidation of the residue, $\{\text{Fe}''(\text{CN})_6\}\text{Fe}'' \text{K}_2$, left in the preparation of hydrocyanic acid.

A third blue compound, $\{\text{Fe}(\text{CN})_6\}\text{FeK}_2 \text{H}_2\text{O}$, isomeric with Williamson's violet, is formed when molecular proportions of a ferrous salt and potassium ferrocyanide are brought together in neutral solution at the ordinary temperature and then oxidised with hydrogen peroxide. It has up to the present been confused with the soluble Prussian blue; it has a greenish-blue colour in aqueous solution, is stable

towards a 5 per cent. solution of ammonium carbonate, but rapidly decomposed by 4 per cent. ammonia. It is completely insoluble in oxalic acid and in aqueous solution is converted by dilute sulphuric acid into an insoluble blue compound. The constitutional formula, $\{\text{Fe}''(\text{CN})_6\}_3\{\text{Fe}'''(\text{OH})\text{KH}\}$, is suggested for this compound.

The cause of the colour of the iron-cyanogen compounds is discussed ; it is pointed out that the colour is associated with the presence of both bivalent and tervalent iron in the same molecule. Similarly, red lead contains both bivalent and tervalent lead ; and the deep indigo-blue sulphur sesquioxide, although the other oxides of sulphur are colourless, also contains sulphur, showing two degrees of valency. This peculiar relation between constitution and colour will be discussed in a later communication.

K. J. P. O.

Some Derivatives of Octahydroanthracene and Perhydroanthracene. MARCEL GODCHOT (*Compt. rend.*, 1905, **141**, 1028—1030. Compare Abstr., 1904, i, 987 ; 1905, i, 201).—*Hexahydroanthrone oxime*, $\text{C}_{14}\text{H}_{16}:\text{N}\cdot\text{OH}$, obtained by heating hexahydroanthrone and hydroxylamine acetate, crystallises from alcohol in small, colourless needles melting at 143° , readily soluble in alcohol, ether, or light petroleum, and reduced by sodium in alcoholic solution to *octahydroanthramine*, $\text{C}_{14}\text{H}_{17}\cdot\text{NH}_2$, a yellow liquid boiling at 182° under 12 mm. pressure and having strongly basic properties, combining with the carbon dioxide of the air ; the *hydrochloride*, $\text{C}_{14}\text{H}_{17}\cdot\text{NH}_2\cdot\text{HCl}$, forms colourless prisms decomposing without fusion at 188° and readily soluble in water or alcohol ; the *picrate* forms yellow needles melting at 212° , readily soluble in alcohol, less so in ether or light petroleum ; the *acetyl* derivative, $\text{C}_{14}\text{H}_{17}\cdot\text{NHAc}$, crystallises from alcohol in beautiful colourless needles melting at 183° , and soluble in benzene, ether, or chloroform. Perhydroanthracene, $\text{C}_{14}\text{H}_{24}$, prepared by reducing anthracene with hydrogen iodide and phosphorus (compare Lucas, Abstr., 1888, 1201), can be obtained more readily by the action of hydrogen iodide and red phosphorus on octahydroanthracene in sealed tubes at 250° or by the direct hydrogenation of octahydroanthracene in the presence of reduced nickel at 180° , a liquid hydrocarbon, probably *dodecahydroanthracene*, $\text{C}_{14}\text{H}_{22}$, being formed at the same time.

M. A. W.

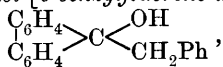
Fluorene Compounds. FRITZ ULLMANN and R. VON WURSTENBERGER (*Ber.*, 1905, **38**, 4105—4110).—9:9-*Diphenylfluorene* [*diphenylbiphenylenemethane*], $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CPh}_2$, prepared by the action of bromobenzene and magnesium on methyl diphenyl-2-carboxylate, crystallises from acetic acid in colourless prisms, melts at 222° (corr.), and boils without decomposition above 400° .

Biphenylenemethylcarbinol [9-*methylfluorene alcohol*], $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CMe}\cdot\text{OH}$, prepared by the action of methyl iodide and magnesium on fluorenone, crystallises from benzene in glistening prisms and melts at 174.5° .

The corresponding *ethyl* compound, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CEt} \cdot \text{OH}$, crystallises from light petroleum and melts at 101° .

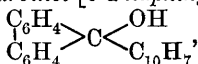
Biphenylenepropylene [*9-ethylidene-fluorene*], $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{C} : \text{CHMe}$, prepared by the action of acetic and hydrochloric acids on the preceding compound, crystallises from acetic acid and melts at 104° .

Biphenylenebenzylcarbinol [*9-benzylfluorene alcohol*],



separates from a mixture of benzene and light petroleum in large crystals and melts at 139° . *Biphenylenephenylethylene* [*9-benzylidene-fluorene*], $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{C} : \text{CHPh}$, separates as a yellow oil which crystallises and melts at 76° .

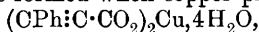
Biphenylene- α -naphthylcarbinol [*9- α -naphthylfluorene alcohol*],



crystallises from a mixture of benzene and light petroleum and melts at 151.5° . It is reduced by zinc and acetic acid to *biphenylene- α -naphthylmethane* [*9- α -naphthylfluorene*], $\text{C}_{23}\text{H}_{16}$, which separates from alcohol in colourless needles and melts at 103.5° . *Biphenylene-p-aminophenyl- α -naphthylmethane* [*9-p-aminophenyl-9- α -naphthylfluorene*], $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{NH}_2 \\ \text{C}_{10}\text{H}_7 \end{smallmatrix}$, prepared by the action of aniline on the carbinol, separates from alcohol in small, white, strongly electric crystals and melts at 145° . The *hydrochloride*, $\text{C}_{29}\text{H}_{21}\text{N} \cdot \text{HCl}$, is a white, crystalline powder and melts and decomposes at $225-230^\circ$.

T. M. L.

Acetylene Linking. FRITZ STRAUS (*Annalen*, 1905, 342, 190—265).—Phenylacetylene, together with copper phenylacetylide and diphenyldiacetylene, are formed when copper phenylpropionate,



is heated. Solutions of sodium phenylpropionate and cupric chloride are mixed and steam passed into the mixture, when the hydrocarbon distils over. If copper phenylpropionate is treated with pyridine or quinoline, only copper phenylacetylide and diphenyldiacetylene are formed.

Copper phenylacetylide dissolves in boiling acetic acid with an orange-yellow coloration, no appreciable quantity of hydrocarbon being evolved. The solution deposits on cooling or on addition of ice-cold water, the *double salt*, $\text{CPh} : \text{CCu} \cdot \text{CH}_3 \cdot \text{CO}_2\text{Cu}$, which crystallises in orange-yellow leaflets; this substance oxidises very readily, its solution in organic solvents being decomposed by contact with air, copper phenylacetylide being formed. If air is passed through its boiling solution in acetic acid, diphenylbuteninene is formed, a reaction which is thought to indicate the presence of more than one hydrocarbon radicle in the molecule of the copper compound.

Diphenyldiacetylene, CPh:C:C:Ph , is prepared by treating copper phenylacetylide with an aqueous solution of potassium ferricyanide made alkaline by potassium hydroxide, or by warming copper phenylpropionate with pyridine; it is crystallised from methyl alcohol and melts at $86-87^\circ$. *Diphenylbuteninene*, CHPh:CH:C:Ph , prepared by dissolving copper phenylacetylide in acetic acid in a flask from which the air has been expelled, boiling, and then sucking air through the mixture, crystallises in colourless prisms melting at $96.5-97^\circ$. The solution in acetic acid becomes blue on the addition of sulphuric acid, and then forms a dichroic, violet-red liquid.

[With RUDOLF MÜLLER.]—In chloroform or carbon disulphide solution, diphenyldiacetylene yields a mixture of stereoisomeric tetrabromides, $\text{CPhBr:CBr:CBr:CPhBr}$, from which the hydrocarbon is regenerated by reduction with zinc dust in acetone solution. It is noteworthy that more than four atoms of bromine cannot be added to the molecule. A *dibromide*, CPhBr:C:C:PhBr (?), is formed as an intermediate product, crystallising in yellow rhombs, melting at 142° . The mixture of tetrabromides melts at $120-140^\circ$, and a *tetrabromide* (m. p. 172°) can be isolated from this mixture by crystallisation from petroleum.

When diphenyldiacetylene in acetic acid is treated with excess of bromine, a *tribromo*-derivative is obtained which is not, as Hollemann thought, a *tribromo*-derivative of the diacetylene, but *tribromo- α -phenylnaphthalene*, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CBr:CBr} \\ | \\ \text{CPh:CBr} \end{smallmatrix}$; it crystallises in yellow nodules melting at 151° . When reduced with alcohol and sodium amalgam, it is converted into *α -phenylnaphthalene*, $\text{C}_{10}\text{H}_7\text{Ph}$, which boils at $192-195^\circ$ under 17 mm. pressure and is oxidised by potassium dichromate and sulphuric acid to *o*-benzoylbenzoic acid. Reduction of the tribromide with zinc dust and acetic acid yields a *dibromo- α -phenylnaphthalene*, $\text{C}_{10}\text{H}_5\text{Br}_2\text{Ph}$, which forms crystals melting at $111-111.5^\circ$.

Diphenyldiacetylene is reduced by boiling in alcoholic solution with zinc dust, light being carefully excluded, to the labile *cis-cis-diphenylbutadiene*, $\begin{smallmatrix} \text{Ph} & & \text{Ph} \\ & \diagdown & / \\ & \text{C:C:C:C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{smallmatrix}$, which crystallises in leaflets or four-

sided plates melting at $70-70.5^\circ$; when exposed to sunlight, this hydrocarbon is transformed into the stable *trans-trans-diphenylbutadiene*, which melts at $142-145^\circ$, or when pure at $150-151^\circ$. As an intermediate product in the reduction, *cis-diphenylbuteninene*, $\begin{smallmatrix} \text{Ph} & & \text{C:Ph} \\ & \diagdown & / \\ & \text{C:C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{smallmatrix}$, is formed; it is a yellow oil, freezing at about 0° and boiling at $187.5-188^\circ$ under 12 mm. pressure; when exposed to sunlight, it is transformed into the stable *trans-diphenylbuteninene* (m. p. 97°) above described. The *cis*-diphenylbuteninene forms with bromine a mixture of tetrabromides from which needles melting and decomposing at 205° , leaflets melting at $135-136^\circ$, and prisms melting and decomposing at 160° can be isolated. The two isomerides with higher melting points are probably identical with the compounds obtained from *trans*-diphenylbuteninene. On treatment

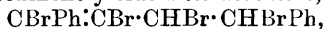
with hydrogen bromide, the same compound is obtained from both the *cis*- and *trans*-isomerides.

cis-trans-Diphenylbutadiene, $\text{Ph} \begin{array}{c} \diagup \\ \text{C} \end{array} \begin{array}{c} \text{H} \\ \diagdown \end{array} : \text{C} : \text{C} : \text{C} \begin{array}{c} \diagup \\ \text{C} \end{array} \begin{array}{c} \text{H} \\ \diagdown \end{array} \text{Ph}$, is prepared from

trans-diphenylbuteninene by reduction with zinc copper couple in alcohol solution in the absence of sunlight, and crystallises in leaflets melting at 150—151°. It is the most unstable of the diphenylbutadienes and passes on transitory exposure to light into the stable *trans-trans*-form.

On bromination, *cis-cis*-diphenylbutadiene yields in chloroform solution a mixture of tetrabromides from which two compounds can be isolated, one crystallising in leaflets melting at 225° and a second crystallising in prisms melting and decomposing at 180°.

trans-Diphenylbuteninene yields a tetrabromide,



when brominated in chloroform solution, which crystallises in leaflets melting and decomposing at 197°; at the same time, a second tetrabromide is formed melting and decomposing at 157—158°. Hydrogen bromide converts the *trans*-diphenylbuteninene into *diphenylbutadiene dibromide*, $\text{C}_{16}\text{H}_{14}\text{Br}_2$, which crystallises in needles melting and decomposing at 142°, and a *bromodiphenylbutadiene*, $\text{C}_{16}\text{H}_{13}\text{Br}$, which crystallises in needles melting at 113.5—114°; the latter monobromoderivative is not changed by hydrogen bromide and is converted by bromine into *bromodiphenylbutadiene dibromide*, $\text{C}_{16}\text{H}_{13}\text{Br}_3$, crystallising in needles melting at 145—147°.

All the diphenylbutadiene bromides are reduced by zinc dust or the zinc copper couple to the stable *trans-trans*-diphenylbutadiene (m. p. 150—151°).

Δ^2 -Diphenylbutene, $\text{CH}_2\text{Ph} \cdot \text{CH} : \text{CH} \cdot \text{CH}_2\text{Ph}$, prepared from diphenylbutadiene, crystallises in needles melting at 45—45.5° and yields a dibromide which, by heating with quinoline, is converted into diphenylbutadiene. When oxidised with potassium permanganate at 0°, $\beta\gamma$ -dihydroxy- $\alpha\delta$ -diphenylbutane, $\text{CH}_2\text{Ph} \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2\text{Ph}$, is obtained as needles melting at 125°. The diphenylbutene can also be prepared by reducing with alcohol and sodium amalgam diphenyl-diacyetylene, *trans*-diphenylbuteninene, *trans-trans*-diphenylbutadiene, and *cis-cis*-diphenylbutadiene.

Δ^2 -Phenylbutene, $\text{CH}_2\text{Ph} \cdot \text{CH} : \text{CHMe}$, is formed from phenylbutadiene by reduction with sodium amalgam and alcohol, but styrene is not reduced under similar treatment. Phenylacetylene is reduced by zinc dust and alcohol to styrene and diphenylbutadiene; with zinc dust and acetic acid, diphenyldiacetylene yields a number of reduction products. Tolane is not attacked by sodium amalgam and alcohol, but by zinc dust and alcohol is converted into *isostilbene*. When oxidised, stilbene yields *isohydrobenzoin*, and *isostilbene*, benzoin.

K. J. P. O.

Action of Ethylene Dibromide on *p*-Nitrosodialkylanilines.

II. HENRY A. TORREY (*Amer. Chem. J.*, 1905, 34, 475—481. Compare Abstr., 1902, i, 755).—Di-*p*-nitrosodimethylaniline-ethylene,

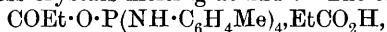
obtained by the action of ethylene dibromide on *p*-nitrosodimethylaniline, is identical with tetramethyldiaminoglyoxime *N*-phenyl ether, described by Pechmann and Schmitz (Abstr., 1898, i, 309). When the reaction takes place in alcoholic solution, tetramethyldiaminoazoxybenzene is produced. By the action of dilute nitric acid on tetraethyldiaminoglyoxime *N*-phenyl ether, tetramethyldiaminoglyoxaldianil is formed, which, when boiled with an alcoholic solution of salicylaldehyde, is converted into *o*-hydroxybenzylidene-*p*-aminodimethylaniline; whilst by the action of benzoyl chloride, benzoyl-*p*-aminodimethylaniline is produced. The dianil yields a bronze-coloured *picrate*, gives a blue precipitate with mercuric chloride, and a blue coloration with dilute solutions of bromine, chlorine, hydrochloric acid, and acyl chlorides.

By the action of ethylene dibromide on *p*-nitrosodiethylaniline, tetraethyldiaminoglyoxime *N*-phenyl ether (Pechmann and Schmitz, *loc. cit.*) and *p*-nitrosodiethylaniline hydrobromide are produced.

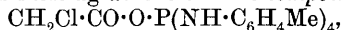
E. G.

New Derivatives of Pentabasic Phosphoric Acid, $P(OH)_5$. PAUL LEMOULT (*Compt. rend.*, 1905, 141, 1241—1244).—The phosphorus alkyloxytetra-anilides of the type $P(OR^1)(NHR)_4$, where R^1 and R represent alkyl and aryl radicles respectively (compare Abstr., 1904, i, 807), condense with acetic or propionic acids to form compounds of the type $COR^1 \cdot O \cdot P(NHR)_4$, which may be regarded as the acetates or propionates of the base $OH \cdot P(NHR)_4$. These compounds form well-defined crystals, usually containing acid of crystallisation, which they lose at 100° ; they are readily decomposed by water or alkalis to form the corresponding phosphoryltrianilides, $PO(NHR)_3$, and by hydrochloric acid to form the corresponding chlorotetra-anilides.

The *o*-toluidine-compound, $OAc \cdot P(NH \cdot C_6H_4Me)_4 \cdot AcOH$, forms beautiful, colourless crystals melting at 221° . The compound,



forms small crystals melting at 203° . The compound,



forms a confused crystalline mass. The 1:3:4-*xylylidine*-compound, $OAc \cdot P(NH \cdot C_6H_3Me_2)_4 \cdot 1.5AcOH$, forms beautiful, colourless spangles several millimetres in dimensions, melting at 210° . The compounds, $OAc \cdot P(NHPh)_4$ and $COEt \cdot O \cdot P(NHPh)_4$, obtained by the action of acetic or propionic acid respectively on trianilinephenylphosphimide, $P(NHPh)_3 : NPh$ (Abstr., 1903, i, 672), crystallise from a mixture of benzene and ether and melt at 206 — 207° and 240° respectively.

M. A. W.

Partial Reduction of Aromatic Dinitro- and Polynitro-derivatives by Electrolytic Methods. KURT BRAND (*Ber.*, 1905, 38, 4006—4015).—*m*-Nitrophenylhydroxylamine can be easily obtained by the electrolytic reduction of *m*-dinitrobenzene in an approximately neutral solution; the cathode cell consists of a porous pot containing the *m*-dinitrobenzene dissolved in aqueous alcohol with a little acetic

acid and sodium acetate. The anode liquid used is 20 per cent. sulphuric acid. The cathode is made of silver gauze and the anode is a perforated lead plate.

m-Nitrophenylhydroxylamine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{OH}$, prepared in this way, separates from hot benzene in thick, yellow crystals, melts at 118 – 119° , and is easily oxidised by alcoholic ferric chloride to *m*-nitronitrosobenzene (Bamberger and Hübner, Abstr., 1904, i, 115); when warmed with dilute sulphuric acid, *m*-nitrophenylhydroxylamine is converted into 2-nitro-4-aminophenol. The substance melting at 178° , described by Wohl (D.R.-P. 84138) as *m*-nitrophenylhydroxylamine, seems to be a transformation product of the latter; its nature is being investigated.

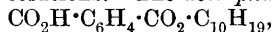
On reducing *m*-dinitrobenzene in alkaline solution, using mercury as the cathode so as to prevent the formation of a solid film on the latter and thus stopping the action, *m*-dinitroazoxybenzene is obtained; the yield is good and the method can be used for preparing the substance. The reduction of *m*-dinitrobenzene in strongly acid solution gives *m*-nitroaniline, the yield being good.

W. A. D.

Hydrogenation Derivatives of Carvacrol. LÉON BRUNEL (*Compt. rend.*, 1905, 141, 1245–1247. Compare Abstr., 1904, i, 158).—When carvacrol is directly hydrogenated in the presence of reduced nickel at 160° , a mixture of two isomeric hexahydrocarvacrols (α - and β -carvacromenthols) is produced; they are probably the two stereoisomerides formed by the hydrogenation of an intermediate ketone, the corresponding carvacromenthone (compare Abstr., 1905, i, 197, 363); when the hydrogenation is effected at 115 – 120° , β -carvacromenthol is the only product.

α -Carvacromenthol is a colourless, oily liquid with an odour of thyme, and boils at 219° .

β -Carvacromenthol, an oily, colourless liquid with an odour of mint, boils at 222° , does not crystallise at -10° , has a sp. gr. 0.918 at 0° , and forms well-defined esters with acids. The *formate*, $\text{HCO}_2 \cdot \text{C}_{10}\text{H}_{19}$, obtained by the direct action of formic acid and the alcohol in the cold, is a colourless, mobile liquid with an agreeable odour like that of camphor, boils at 229° , and has a sp. gr. 0.954 at 0° . The *acetate*, $\text{OAc} \cdot \text{C}_{10}\text{H}_{19}$, prepared by heating acetic acid and the alcohol in sealed tubes at 130° , is a colourless, mobile liquid with a strong odour, which boils at 231.5° , does not crystallise at -10° , and has a sp. gr. 0.933 at 0° . The *acid succinate*, $\text{CO}_2\text{H} \cdot \text{C}_2\text{H}_4 \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19}$, prepared by heating the alcohol with succinic anhydride at 100° , crystallises from light petroleum in thin, colourless, odourless needles melting at 74° and soluble in dilute alkali solutions. The *acid phthalate*,



crystallises from alcohol in large, colourless, odourless crystals melting at 136° and soluble in alkali solutions.

M. A. W.

Action of Phosphorus Pentachloride on β -Naphthol. E. BERGER (*Compt. rend.*, 1905, 141, 1027–1028).—At temperatures below 130° , phosphorus pentachloride reacts with β -naphthol to form β -dinaphthyl ether, but when the temperature is raised to 135 – 140° and

the heating continued for twenty-four hours, a mixture in the proportion $3\text{PCl}_5 : 2\text{C}_{10}\text{H}_7\text{OH}$ yields 30 per cent. of β -chloronaphthalene (compare Cleve, Abstr., 1876, ii, 81; Rimarenko, Abstr., 1876, ii, 297), together with small quantities of 1:2-, 2:4-, 2:6-, and 2:8-dichloronaphthalenes, $\beta\beta$ -dinaphthylene oxide, and di- β -naphthyl hydrogen phosphate, melting at 143° . M. A. W.

2:3-Dihydroxyanthracene. KASIMIR LAGODZINSKI (*Annalen*, 1905, 342, 90—111. Compare this vol., i, 98).—2:3-Dihydroxyanthracene, which has been prepared in order to procure 2:3-anthraquinone, is obtained from the dimethyl ether of hystazarin, which is synthesised from veratrole.

o-3':4'-Dimethoxybenzoylbenzoic acid, $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, prepared by warming a carbon disulphide solution of veratrole with phthalic anhydride and aluminium chloride, crystallises in colourless leaflets melting at 233° and is soluble in concentrated sulphuric acid with a blood-red coloration; the ammonium salt forms white needles and the silver salt white crystals. The acid does not react with hydroxylamine, but with phenylhydrazine yields 2-phenyl-4-veratryl-phthalazone, $\begin{matrix} \text{CO} \cdot \text{C}_6\text{H}_4 \\ \text{NPh} - \text{N} \end{matrix} \gg \text{C} \cdot \text{C}_6\text{H}_3(\text{OMe})_2$, which crystallises in yellow needles melting at 189° .

The dimethyl ether of hystazarin (2:3-dimethoxyanthraquinone), $\text{C}_6\text{H}_4 \begin{matrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{matrix} \text{C}_6\text{H}_2(\text{OMe})_2$, is formed when dimethoxybenzoylbenzoic acid is warmed with concentrated sulphuric acid, and crystallises in golden-yellow needles melting at 237° ; it yields a blood-red solution in sulphuric acid. Prolonged heating at 100° with sulphuric acid converts the dimethyl ether into the monomethyl ether, $\text{OH} \cdot \text{C}_{14}\text{H}_6\text{O}_2 \cdot \text{OMe}$, which crystallises in orange-yellow leaflets melting at 236° . The complete hydrolysis of the ether to hystazarin is best effected by heating with hydrobromic acid of sp. gr. 1.49 under pressure at 180° . On reduction with zinc dust and 5 per cent. ammonia, the dimethyl ether of hystazarin is converted into 2:3-dimethoxyanthracene, $\text{C}_{14}\text{H}_8(\text{OMe})_2$, crystallising in colourless leaflets or needles melting at 204° ; the alcoholic solution has a blue fluorescence, and the solution in sulphuric acid an orange-yellow coloration; the picrate is dark brown in colour; in acetic acid solution it is converted into a polymeride melting at 314° , and in alcoholic solution it is oxidised to the corresponding anthraquinone. When warmed with hydriodic acid (b. p. 127°), the dimethoxyanthracene yields 2:3-dihydroxyanthracene, which crystallises in straw-yellow leaflets decomposing at 180 – 192° . 2:3-Diacetoxyanthracene forms pale yellow crystals melting at 155 – 160° .

Attempts to oxidise this dihydroxyanthracene to the corresponding 2:3-dihydroxyanthraquinone were not successful.

When dimethoxyanthracene is heated in acetic acid solution with hydriodic acid of sp. gr. 1.70, a compound, $\text{C}_{30}\text{H}_{20}\text{O}_4$, of unknown constitution is formed; it crystallises in yellow leaflets decomposing at about 260° . It forms in sulphuric acid an orange-yellow solution which becomes blood-red on heating; its solution in alkali hydroxides is yellow. It can be methylated by methyl sulphate and potassium

hydroxide and acetylated by acetic anhydride. With ether, it forms the compound, $C_{30}H_{20}O_4 \cdot 2OEt_2$, which crystallises in greenish-yellow plates.

K. J. P. O.

Aromatic Sulphine Bases. FRIEDRICH KEHRMANN and A. DUTTENHÖFER (*Ber.*, 1905, **38**, 4197—4199).—The *platinichloride* of diphenylmethylsulphine, $(C_{13}H_{13}S)_2PtCl_6$, forms a yellowish-white, crystalline precipitate melting at 169.5° ; the *dichromate* separates as a yellow, flocculent precipitate which rapidly becomes green and decomposes, forming a substance crystallising in orange needles and melting at 129° . *Di- α -naphthylmethylsulphine platinichloride*, $(C_{21}H_{17}S)_2PtCl_6$, forms a flesh-coloured powder and melts at 162 — 163° ; the *aurichloride* is yellow and the *dichromate* is orange. *Di- β -naphthylmethylsulphine platinichloride* melts at 136 — 146° .

E. F. A.

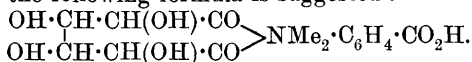
Behaviour of Esters of Organic Acids when heated with Orthophosphoric Acid. PAUL N. RAIKOW and P. TISCHKOW (*Chem. Zeit.*, 1905, **29**, 1268—1273).—The combined action of heat and orthophosphoric acid on the methyl esters of various organic acids was studied with the object of determining whether or not the ester lost carbon dioxide, leaving the methyl group attached to the rest of the molecule. The acid used was first dehydrated by heating 60 c.c. of syrupy phosphoric acid of sp. gr. 1.7 to 200° in a round-bottomed flask of 200 c.c. capacity; after cooling to below 100° , a measured quantity of the ester was added and the mixture was then boiled over iron gauze. The flask was attached to a reflux condenser, the upper end of which was connected by an india-rubber tube to one limb of a U-tube containing 50 c.c. of concentrated sulphuric acid; the other limb was connected to an apparatus for determining the amount of carbon dioxide evolved by measuring the water which it displaced from a wide-mouthed bottle of 2 litres capacity filled with water. The boiling was continued until the evolution of gas had ceased. The gas remaining in the bottle was examined for carbon dioxide and carbon monoxide; the object of the U-tube with strong sulphuric acid was to absorb any dimethyl ether which might be formed. The following compounds were examined in this way. The methyl esters of benzoic, *o*-, *m*-, and *p*-toluic, *o*-, *m*-, and *p*-chlorobenzoic, *p*-bromobenzoic, *o*-iodobenzoic, *o*-, *m*-, and *p*-aminobenzoic, *o*-, *m*-, and *p*-nitrobenzoic, salicylic, *m*- and *p*-hydroxybenzoic, 2-hydroxy-3-methylbenzoic, 2-hydroxy-4-methylbenzoic, 2-hydroxy-5-methylbenzoic, 2:4-dihydroxybenzoic, gallic, anisic, vanillic, 3-chloro-2-nitrobenzoic, 3:5-di-iodo-2-hydroxybenzoic, 6-nitro-2-hydroxybenzoic, 4-nitro-2-hydroxybenzoic, phthalic, isophthalic, tetrachlorophthalic, *o*- and *p*-nitrophthalic, α - and β -naphthoic, *p*-hydroxynaphthoic, phenylacetic, hydrocinnamic, and cinnamic acids; also the ethyl esters of propionic and butyric acids, the phenyl esters of benzoic and salicylic acids, as well as the following two free acids, terephthalic and dichlorophthalic. The following conclusions are drawn from the experimental results:—(1) Except in the case of methyl *p*-chlorobenzoate, the methyl of the ester group was never observed to replace the $-CO_2Me$ group, and the method is therefore of no use for the introduction of a methyl group into the benzene nucleus. (2) The methyl group was commonly split off in the form

of dimethyl ether; in the case of aromatic hydroxy-acids it frequently wandered from the carboxyl group to the phenolic hydroxyl group in the ortho- or para-position. The ethyl group was split off from the two ethyl esters examined in the form of ethylene. (3) With the exception of the esters of cinnamic and *o*-nitrocinnamic acids, no esters containing the $\text{-CO}_2\text{Me}$ group attached to an aliphatic complex gave off carbon dioxide. (4) The introduction of substituting groups into benzoic acid reduces the stability of the $\text{-CO}_2\text{Me}$ group. (5) The stability of the $\text{-CO}_2\text{Me}$ group is influenced both by the nature of the substituting group and by its position in the ring. (6) The hydroxyl and the amino-groups have the greatest influence. (7) In naphthoic acids, the second benzene ring acts on the $\text{-CO}_2\text{Me}$ like a substituting group, but exerts a greater influence in the case of the α - than in the case of the β -acid. (8) Unlike all other substituting groups, the introduction of a second $\text{-CO}_2\text{Me}$ increases the stability of the CO_2Me group.

P. H.

The Glucoside Structure of Conjugated Glycuronic Acids.

HERMANN HILDEBRANDT (*Beitr. chem. Physiol. Path.*, 1905, 7, 438—454. Compare Abstr., 1901, ii, 614; Neuberg and Neimann, 1905, i, 412).—Emulsin has no action on the glycuronic acid derivative of *p*-dimethylaminobenzoic acid; the derivative probably has not a glucosidic structure and the following formula is suggested:



p-Benzobetaine does not couple with glycuronic acid in the animal system; the greater part is eliminated unaltered and a small portion is converted into mono- and di-methyl-*p*-aminobenzoic acids.

The glucosides of glycerol and benzyl alcohol (E. Fischer, Abstr., 1895, i, 6) are hydrolysed by both emulsin and yeast.

Glycuronic acid itself is decomposed by yeast or zymase, volatile acids are formed, and the solution loses its reducing properties.

When syringinaldehyde is administered to dogs, both free syringic acid and its compound with glycuronic acid are found in the urine.

When syringin is injected subcutaneously in dogs, Körner's glucosyringic acid (Abstr., 1889, 159) and syringaglycuronic acid are found in the urine. Both acids are hydrolysed by emulsin. When coniferin is administered in the same way, no free vanillic acid can be found in the urine, but potassium vanillinglycuronate can be isolated. This is hydrolysed by emulsin.

J. J. S.

Oxidation of 4-Nitro-6-amino-*m*-xylene. GIORGIO ERRERA and RAFFAELE MALTESE (*Gazzetta*, 1905, 35, ii, 370—383).—When oxidised with potassium permanganate, 4-nitro-6-diacetyl-amino-*m*-xylene yields a mixture of 4-nitro-6-aminoisophthalic acid, 4-nitro-6-amino-*m*-toluic and 6-nitro-4-amino-*m*-toluic acids and their monoacetyl derivatives.

6-Nitro-4-acetyl-amino-*m*-toluic acid, $\text{C}_{10}\text{H}_9\text{O}_5\text{N}_2$, separates from alcohol or ethyl acetate in sulphur-yellow, triclinic crystals [$a:b:c = 1.6623:1:1.0340$; $\alpha = 79^\circ 40'$, $\beta = 64^\circ 4'$, and $\gamma = 105^\circ 33'$], melts and decomposes at $223\text{--}225^\circ$, and dissolves slightly in water, benzene, or

xylene, readily in acetic acid. The corresponding *potassium* salt was prepared and analysed.

4-Nitro-6-acetyl-amino-m-toluic acid, $C_{10}H_{10}O_5N_2$, crystallises from alcohol in pale straw-yellow plates melting and decomposing at $254-255^\circ$ and is less soluble than the acid just described in all solvents except water; its *potassium* salt was analysed.

6-Nitro-4-amino-m-toluic acid, $C_8H_8O_4N_2$, separates from alcohol or ethyl acetate in shining, red crystals melting and decomposing at $239-240^\circ$ and dissolves slightly in water or benzene.

4-Nitro-6-amino-m-toluic acid, $C_8H_8O_4N_2$, crystallises from water in golden-yellow needles which, on rapid heating in a capillary tube, melt at about 235° ; it dissolves readily in alcohol or ethyl acetate and slightly in benzene. On heating the acid or its acetyl derivative with concentrated sulphuric acid, it yields 4-nitro-*o*-toluidine. The *methyl* ester, $C_9H_{10}O_4N_2$, separates from methyl alcohol in either needles or hard crystals of a pale yellowish-grey colour, and melts at 169° .

4-*o*-p-Dinitroanilino-6-nitro-m-toluic acid, $C_{14}H_{10}O_8N_4$, crystallises from acetic acid in yellow needles which melt, after blackening, at 298° ; it is only slightly soluble in the ordinary solvents and gives red salts.

1:3:8-Trinitro-7-methylacridone, $C_{13}NH_5Me(NO_2)_3$, prepared by heating the preceding acid or its ammonium salt with sulphuric acid and subsequently pouring the mass into water, separates from acetic acid in large, dark brown crystals or from benzene in orange-brown needles which melt, after blackening, at 253° ; it dissolves slightly in alcohol and to a greater extent in xylene.

T. H. P.

[Claisen's Cinnamic Acid Synthesis.] ARTHUR MICHAEL (*Ber.*, 1905, 38, 4137).—Polemical. A reply to Störmer and Kippe (*Abstr.*, 1905, i, 777).

J. J. S.

Synthesis of Tyrosine. PETER W. LATHAM (*Lancet*, 1905, ii, 1757).—A new method of synthesising tyrosine from hydrogen cyanide and *p*-hydroxybenzaldehyde is described. It is pointed out that, in the body, adenine, an isomeride of hydrogen cyanide, may take the place of the latter substance in tyrosine formation.

W. D. H.

Synthesis of Amino-acids of Proteid Origin. LOUIS HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1906, 142, 48—49. Compare *Abstr.*, 1905, i, 178, 264, 332).—The symmetrical *p*-hydrocoumaric acid derivative of carbamide, $CO[NH \cdot CH(CO_2H) \cdot CH_2 \cdot C_6H_4 \cdot OH]_2$, precipitated when a slow stream of carbonyl chloride is passed into an aqueous solution of the sodium salt of tyrosine, is very sparingly soluble in water, more soluble in alcohol, from which solution it is precipitated by water in the form of flakes resembling proteid matter. The dry powder darkens at 150° , melts at 240° , and gives a red colour with Millon's reagent. The *p*-hydrocoumaric acid derivative of phenyl-carbamide, $NHPh \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot C_6H_4 \cdot OH$, prepared by the action of phenylcarbimide on the sodium salt of tyrosine, is very

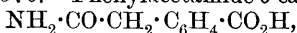
sparingly soluble in water, can be crystallised from alcohol, melts and decomposes at 194° , and reacts with Millon's reagent. M. A. W.

Conductivity Measurements with Organic Acids. JOSEF HANS SÜSS (*Monatsh.*, 1905, **26**, 1331—1342. Compare Wegscheider, *Abstr.*, 1902, i, 617; and following abstract).—With $\mu_{\infty} = 375$, nitro-opianic acid has $K\ 0.000291$; a week-old solution has a 20 per cent., a solution which has been heated on the water-bath for one hour a 5 per cent., greater conductivity.

5-Nitro-2-aldehydobenzoic acid has $K\ 0.0100$ with $\mu_{\infty} = 378$. 3-Nitro-2-aldehydobenzoic acid has $K\ 0.000130$ with $\mu_{\infty} = 378$. Nitro-hemipinic acid $[(\text{CO}_2\text{H})_2 : (\text{OMe})_2 : \text{NO}_2 = 1 : 2 : 3 : 4 : 6]$ has $K\ 2.1$ with $\mu_{\infty} = 374$; at the dilution $v = 256$, it shows marked dibasic dissociation, which is not observed with hemipinic acid at the dilution $v = 1000$. The dissociation constant for the second hydrogen atom is $s \times 10^6 = 208$ or 218.

Aminoterephthalic acid has $K\ 0.0265$ with $\mu_{\infty} = 377$, whilst its 1-methyl ester has $K\ 0.00552$ with $\mu_{\infty} = 376$. Methylaminoterephthalic acid has $K\ 0.030$ with $\mu_{\infty} = 376$. Acetylamino-terephthalic acid has $K\ 0.098$ with $\mu_{\infty} = 375$. A slightly impure specimen of 1-methyl hydrogen acetylamino-terephthalate had $K\ 0.07$ with $\mu_{\infty} = 374.4$. Acetylmethylaminoterephthalic acid has $K = 0.126$ with $\mu_{\infty} = 374.4$.

Homophthalic acid has $K\ 0.0190$ with $\mu_{\infty} = 376.5$; the α -mono-methyl ester has $K\ 0.00434$ with $\mu_{\infty} = 375.3$; the β -monomethyl ester has $K\ 0.00764$ with $\mu_{\infty} = 375.3$. The α -monoethyl ester has $K\ 0.0046$ with $\mu_{\infty} = 374.6$; the β -monoethyl ester has $K\ 0.00708$ with $\mu_{\infty} = 374.6$. 2-Carbamidophenylacetic acid, $\text{NH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, has $K\ 0.0050$ with $\mu_{\infty} = 376$. Phenylacetamide- α -carboxylic acid,



has $K\ 0.0089$ with $\mu_{\infty} = 376$.

Phthalonic acid resembles pyruvic acid in that it is a strong acid, the affinity constant of which diminishes rapidly as the dilution increases; it has $K\ 2.14$ at the dilution $v = 128$; $K\ 1.91$ at $v = 256$; $K\ 1.44$ at $v = 512$; and $K\ 1.10$ at $v = 1024$. Methyl hydrogen phthalonate, $\text{CO}_2\text{Me} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, prepared by partial hydrolysis of the dimethyl ester, as also by the action of methyl alcohol on the acid, has $K\ 0.015$ with $\mu_{\infty} = 375.7$.

Phenylitaconic acid, $\text{CHPh} \cdot \text{C}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, has $K\ 0.0137$ with $\mu_{\infty} = 375$; it shows no distinct dibasic dissociation. G. Y.

Constitution of α -Aldehydo-acids in Aqueous Solution. RUDOLF WEGSCHEIDER (*Monatsh.*, 1905, **26**, 1231—1234. Compare Wegscheider, *Abstr.*, 1902, ii, 494; 1903, i, 562).—The affinity constants of α -phthalaldehydic, 5-nitro-2-aldehydobenzoic, 3-nitro-2-aldehydobenzoic, and nitro-opianic acids are smaller than those of the corresponding acids without the aldehyde group. These aldehydo-acids must exist in aqueous solution, to a greater or less extent, as the *pseudo*-form, $\text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CO} \cdot \text{O}$, whilst opianic acid, the affinity constant of which is ten times that calculated for the corresponding

acid without the aldehyde group, must exist in aqueous solution entirely in the normal or carboxylic form. A comparison of the affinity constants of *o*-phthalaldehydic and opianic acids shows that methoxy-groups in the *ortho*- and *meta*-positions prevent the formation of the *pseudo*-form. The influence of a nitro-group in the *meta*-position to the carboxyl-group on the formation of the *pseudo*-form is only slightly favourable if the nitro- and aldehyde-groups are in the *para*-position, but highly favourable if these groups are in the *ortho*-position to one another. G. Y.

Action of Diazomethane on Aldehydo-acids and Aldehydes.

HANS MEYER (*Monatsh.*, 1905, **26**, 1295—1301. Compare Abstr., 1905, i, 133).—Diazomethane is estimated by shaking its solution with an equal volume of *N*/10 aqueous hydrochloric acid, whereby it is converted into methyl chloride completely in a few seconds, and titrating the excess of acid with *N*/10 alkali hydroxide.

Opianic acid and diazomethane interact energetically to form methyl opianate.

The action of diazomethane on bromo-opianic acid, or of methyl iodide on the silver salt at the laboratory temperature, leads to the formation of *methyl bromo-opianate*, $C_{11}H_9O_5Br$, which crystallises from benzene and melts at 105—106°. The ψ -*methyl* ester, formed by the action of thionyl chloride or of boiling methyl alcohol and sulphuric acid on the acid, crystallises in needles and melts at 109—110°. A mixture of equal amounts of the isomeric esters melts at 70° (compare Bistrzycki and Fink, Abstr., 1898, i, 427).

The action of diazomethane on nitro-opianic acid leads to the formation of the normal ester (Wegscheider, Kuśy von Dúbrav, and Rušnov, Abstr., 1904, i, 59).

These aldehydo-acids have therefore the normal constitution when anhydrous (compare Wegscheider, preceding abstract), but whilst opianic and bromo-opianic acids give an intense blue coloration with congo-red, and have therefore the normal constitution in aqueous solution, nitro-opianic acid functions in aqueous solution as a ψ -acid, as it is entirely without action on the indicator (compare Lobry de Bruyn, Abstr., 1899, i, 861).

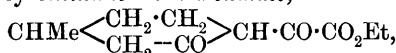
Diazomethane does not interact with benzaldehyde or heptoic aldehyde, but evolves nitrogen slowly in contact with the three nitro-benzaldehydes; *o*-nitrobenzaldehyde yields a brown *oil*, which distils apparently without change; *m*-nitrobenzaldehyde yields a *liquid* and a *solid* product; the latter crystallises in colourless needles, melts at 76°, forms an orange-yellow *hydrazone* melting at 127°, on oxidation by permanganate gives *m*-nitrobenzoic acid, but is not identical with *m*-nitroacetophenone, as it is odourless and dissolves in boiling aqueous potassium hydroxide, forming a reddish-yellow solution; *p*-nitrobenzaldehyde yields two *products* melting at 62—65° and at 84° respectively. The more fusible substance, $C_8H_7O_3N$, dissolves in hot aqueous potassium hydroxide to form a rose-coloured solution changing to yellow, and on oxidation yields *p*-nitrobenzoic acid.

Diazomethane and *p*-chlorobenzaldehyde interact to form a solid *product* which melts at a high temperature. G. Y.

Syntheses by means of the Carboxylic Esters of Cyclic Ketones. Synthesis of Menthone from Methylhexanone. ARTHUR KÖTZ and LUDWIG HESSE (*Annalen*, 1905, **342**, 306—328).—

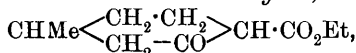
Since the hydroaromatic β -ketocarboxylic acids, such as cyclohexanone-*o*-carboxylic acid, $\text{CH}_2\langle\text{CH}_2\text{---CO}\rangle\text{CH}\cdot\text{CO}_2\text{H}$, would be valuable for synthetical purposes, attempts have been made to prepare such acids with readiness. Endeavours to bring about an internal condensation of esters of dibasic acids in a manner analogous to the formation of ethyl acetoacetate or to condense cyclic ketones with ethyl carbonate led to no result. On the other hand, with ethyl oxalate the ketones yielded ethyl keto-*o*-oxalates.

Ethyl 1-methylcyclohexane-3-one-4-oxalate,



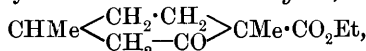
is prepared from methylhexanone and ethyl oxalate and sodium wire in the presence of light petroleum; the mixture is treated with water and the aqueous solution acidified and extracted with ether, the ketonic ester being finally purified in the form of its copper salt; it is a colourless liquid boiling at 163° under 12 mm. pressure, and has a sp. gr. 1.0903 at 15° . The copper salt, $\text{C}_{22}\text{H}_{30}\text{O}_8\text{Cu}$, forms crystals melting at 153° ; the semicarbazone melts at above 245° . 1-Methylcyclohexane-3-one-4-oxalic acid, prepared from the ester by hydrolysis with 10 per cent. sodium hydroxide, melts and decomposes at 132° . The semicarbazone melts at above 245° . When the ester is warmed with aniline, a compound, $\text{CHMe}\cdot\text{CH}_2\cdot\text{C}\cdot\text{NPh}\cdot\text{CO}$
 $\text{CH}_2\text{---CH}_2\cdot\text{C}\text{---}\text{C}\cdot\text{NPh}$, derived from hexahydroindole, is obtained, crystallising in needles melting at 162.5° .

Ethyl 1-methylcyclohexane-3-one-4-carboxylate,



prepared by heating the ester just described under reduced pressure at $150\text{--}220^\circ$, is a colourless oil boiling at 123.5° under 13 mm. and at 165° under 100 mm. pressure, and has a sp. gr. 1.057 at 14° ; the copper salt is an olive-green powder melting at 155° . With phenylhydrazine, the ester gives a compound, $\text{CHMe}\cdot\text{CH}_2\cdot\text{C}\text{---}\text{NH}$
 $\text{CH}_2\text{---CH}_2\cdot\text{C}\cdot\text{CO}\cdot\text{NPh}$, derived from hexahydro-1:2-benzodiazine, which forms crystals melting at $243\text{--}245^\circ$. With ammonia, the ester yields ethyl 3-amino-1-methylcyclohexane-4-carboxylate, $\text{CHMe}\langle\text{CH}_2\text{---CH}_2\rangle\text{C}(\text{NH}_2)\cdot\text{CO}_2\text{Et}$, which forms crystals melting at 67° .

Ethyl 1-dimethylcyclohexane-3-one-1-carboxylate,



prepared from ethyl methylcyclohexanonecarboxylate by treatment with sodium ethoxide and methyl iodide, is an oil boiling at $120\text{--}122^\circ$ under 12 mm. pressure and has a sp. gr. 1.0189 at 19° .

Ethyl 1-methyl-4-isopropylcyclohexane-3-one-4-carboxylate, prepared

in analogous manner, is an oil boiling at 135—137° under 10 mm. pressure, and has a sp. gr. 1·009 at 14°. The *semicarbazone* melts at 144—145°. When this ester is hydrolysed by boiling alcoholic potassium hydroxide, menthone is obtained, melting at 206—208°, and feebly dextrorotatory; it yields a semicarbazone melting at 184—185°.

K. J. P. O.

Tautomerism. III. Apparent Case of Desmotropy. PAUL RABE and DAVID SPENCE (*Annalen*, 1905, 342, 328—355. Compare Abstr., 1901, i, 33, and 1904, i, 749).—The relation between the “acid” and “neutral” forms of Hagemann’s ester (Abstr., 1893, i, 393), which the authors (Abstr., 1905, i, 348) have shown to be ethyl 1-methyl-*cyclo*- Δ^6 -hexene-5-one-2-carboxylate, has been investigated. The conditions under which the isomerides are prepared do not point to their being tautomeric, and the tautomerism, if it exists, cannot be due to the carbonyl group but rather to the carbethoxyl group. To throw light on these phenomena, ethyl phenylmethylcyclohexanonecarboxylate, methylcyclohexanonecarboxylate, and dimethylcyclohexanonecarboxylate have been prepared. It has been found that two desmotropic isomerides do not exist, but that the esters can be separated into two fractions which show a gradual difference in chemical and physical properties. The cause of these observations will be discussed later.

Ethyl 1-methyl-*cyclo*- Δ^6 -hexene-5-one-2-carboxylate (*loc. cit.*) boils at 157—159° under 19—21 mm. pressure and has a sp. gr. 1·0775—1·0783 at 20°/4° and a molecular refraction M_{Na} 48·96—49·02. When shaken with 10 per cent. sodium hydroxide at a low temperature, two fractions are obtained; the soluble fraction, the “acid” ester, boils at 160—163° under 24 mm. pressure and has a sp. gr. 1·0701 at 20°/4° and M_{Na} 49·32; an insoluble fraction, the “neutral” ester, boils at 163° under 24 mm. pressure and has a sp. gr. 1·0856 at 20°/4° and M_{Na} 48·27. Both fractions are soluble in concentrated sodium hydroxide, and both give a reaction with ferric chloride. Knoevenagel’s ethyl 1:3-dimethyl-*cyclo*- Δ^6 -hexene-5-one-2-carboxylate behaves in a similar manner; the ethyl 4-hydroxy-2:6-dimethylbenzoate obtained from it by Noyes is readily hydrolysed by alcoholic potassium hydroxide, yielding 4-hydroxy-2:6-dimethylbenzoic acid, which crystallises in six-sided plates melting and decomposing at 185°.

Ethyl 1-methyl-3-phenylcyclo- Δ^6 -hexene-5-one-2-carboxylate,



prepared by heating ethyl methylphenylcyclohexanonecarboxylate with sodium ethoxide in alcoholic solution, crystallises in four-sided plates melting at 55°; it dissolves but sparingly in 10 per cent. sodium hydroxide, and only gives a colour with ferric chloride after prolonged boiling. The *semicarbazone* crystallises in needles melting at 158—161°.

K. J. P. O.

Preparation of Chloro-derivatives of Indigotin. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 160817).—When indigotin is chlorinated in absence of water, in the dry state or in indifferent solvents, the chlorine does not enter the nucleus, and only unstable

products are obtained. Stable chloro-derivatives of indigotin are obtained, however, when indigotin is suspended in phosphorus oxychloride or sulphuryl chloride, a little iodine being preferably added, and chlorine passed through the well-cooled liquid. The product may be poured on to ice or the volatile compound removed by distillation.

C. H. D.

6:6'-Dinitroindigotin. JULIUS SCHWARZ (*Monatsh.*, 1905, 26, 1253—1263. Compare Baeyer, *Abstr.*, 1879, 937).—5-Nitrophenylglycine-2-carboxylic acid, $C_9H_8O_6N_2$, is obtained in a yield of 70 per cent. of the theoretical by boiling five parts of 4-nitro-2-aminobenzoic acid with 10.5 parts of chloroacetic acid and 13.5 parts of sodium carbonate in aqueous solution in a reflux apparatus for eight hours. It crystallises in long, slender, yellow needles, commences to blacken at 225° , melts and decomposes at 240 — 242° , is readily soluble in alcohol, but only moderately so in acetone, light petroleum, or hot water, yields a reddish-brown, flocculent precipitate, and when heated in a tube sublimes and decomposes partially. The potassium hydrogen salt, $C_9H_7O_6N_2K$, crystallises in microscopic, red needles; the silver salt, $C_9H_6O_6N_2Ag_2$, is obtained as an orange, voluminous precipitate.

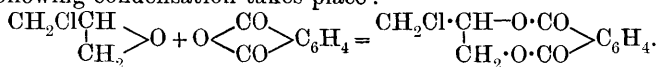
5-Nitroanilodiacetic-2-carboxylic acid, $C_{10}H_{10}O_8N_2$, is obtained as a by-product in the preparation of 5-nitrophenylglycine-2-carboxylic acid; it crystallises from concentrated hydrochloric acid in long, slender, almost white needles, melts and decomposes at 177° , and forms a potassium salt as a yellow precipitate.

1:3-Diacetyl-6-nitroindoxyl, $NO_2 \cdot C_6H_3 \left\langle \begin{smallmatrix} C(OAc) \\ N_{Ac} \end{smallmatrix} \right\rangle CH$, is formed by heating 5-nitrophenylglycine-2-carboxylic acid with sodium acetate and acetic anhydride; it crystallises from alcohol in large, yellow needles, melts at 190° , is almost insoluble in water, but moderately soluble in alcohol, ether, acetone, benzene, or light petroleum, dissolves in warm aqueous sodium carbonate to form a dark green, in concentrated sulphuric acid to form a dark blue, solution, and when warmed with concentrated sulphuric acid yields 6:6'-dinitroindigotin, $C_{16}H_8O_8N_4$. This is obtained in microscopic, round, dark blue granules, is insoluble in water, almost insoluble in hydrochloric or acetic acids, alcohol, ether, benzene, or light petroleum, is slightly soluble in acetone, and dissolves in hot aniline to form a dark green, in phenol, naphthalene or hot nitrobenzene to form dark blue solutions; when heated in a glass tube, it sublimes, whilst on platinum foil it evolves violet vapours and detonates slightly. On reduction with zinc and hydrochloric acid, it yields 6:6'-dinitroindigo-white, and on further reduction 6:6'-diaminoindigo-white, which is oxidised by the atmospheric oxygen to 6:6'-diaminoindigotin. This is distinguished from 6:6'-dinitroindigotin by its solubility in acetic acid, forming a green solution.

G. Y.

Condensation of Epichlorohydrin with Phthalic Anhydride in Presence of Tertiary Bases. ARTHUR WEINSCHENK (*Chem. Zeit.*, 1905, 29, 1311).—When molecular proportions of epichlorohydrin and phthalic anhydride are warmed together over the water-bath in the

presence of a small quantity of dimethylaniline or dimethyltoluidine, the following condensation takes place :



The resulting chloromethylglycol phthalate is a solid below 20° , but between 20° and 30° it assumes a fatty consistency; it is insoluble in water, dissolves with difficulty in alcohol or ether, and is readily soluble in epichlorohydrin. When pyridine is used as the condensing agent, the reaction becomes violent and the mixture rapidly darkens.

P. H.

Butadiene Compounds. XII. Yellow Nitrotriphenylfulgenic Acids and their Red Fulgides. HANS STOBBE and ALBERT KÜLLENBERG (*Ber.*, 1905, 38, 4081—4087).—*Sodium* α -*o*-nitrophenyl- $\delta\delta$ -diphenylfulgenate, $\text{C}_{24}\text{H}_{15}\text{O}_6\text{NNa}_2$, formed by the action of sodium ethoxide on *o*-nitrobenzaldehyde and ethyl $\gamma\gamma$ -diphenylitaconate in absolute alcoholic solution, crystallises in glistening leaflets from water, or in yellow, monoclinic prisms from 50 per cent. alcohol. The acid, $\text{CPh}_2\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, $\text{C}_{24}\text{H}_{15}\text{O}_6$, crystallises from alcohol in yellow needles, loses $\text{C}_2\text{H}_5\text{O}$ at 105° , commences to become red at 180° , and melts and evolves gas at 223 — 224° . The *piperidine* salt, $\text{C}_{24}\text{H}_{17}\text{O}_6\text{N}, 2\text{C}_5\text{H}_{11}\text{N}$, crystallises in yellow needles and melts and decomposes at 201 — 202° .

α -*o*-Nitrophenyl- $\delta\delta$ -diphenylfulgide, $\text{CPh}_2\cdot\text{C}\cdot\text{CO} > \text{O}, \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{C}\cdot\text{CO} > \text{O}$, formed

by boiling the acid with acetyl chloride for four hours, is obtained on slow evaporation of the solution in large, pleochroic, monoclinic crystals; it crystallises from a mixture of chloroform and alcohol in blood-red leaflets, from chloroform alone in yellow needles containing chloroform, which is lost gradually on exposure to air, the crystals changing into an orange-red powder; the three modifications melt at 207 — 208° . Its behaviour towards water, alkali hydroxides, and piperidine is the same as that of dibenzylidenesuccinic anhydride (Stobbe, Naoum, and Kautzsch, *Abstr.*, 1904, i, 589); when oxidised, it yields benzophenone and *o*-nitrobenzoic acid.

α -*m*-Nitrophenyl- $\delta\delta$ -diphenylfulgenic acid is obtained in the form of its sodium salt, $\text{C}_{24}\text{H}_{15}\text{O}_6\text{NNa}_2$, by digesting *m*-nitrobenzaldehyde and ethyl $\gamma\gamma$ -diphenylitaconate with sodium ethoxide in absolute alcoholic solution; this crystallises in yellow leaflets. The acid, $\text{C}_{24}\text{H}_{17}\text{O}_6\text{N}$, crystallises in white leaflets or prisms from ether, in yellow leaflets from acetic acid, and melts and decomposes at 221 — 222° . The *piperidine* salt, $\text{C}_{24}\text{H}_{17}\text{O}_6\text{N}, 2\text{C}_5\text{H}_{11}\text{N}$, forms yellow needles and melts and decomposes at 177 — 178° .

α -*m*-Nitrophenyl- $\delta\delta$ -diphenylfulgide, $\text{C}_{24}\text{H}_{15}\text{O}_5\text{N}$, crystallises from a mixture of chloroform and alcohol in orange-red, slender needles, or from benzene in stellate groups of pleochroic, monoclinic prisms, and melts at 194 — 195° .

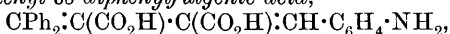
α -*p*-Nitrophenyl- $\delta\delta$ -diphenylfulgenic acid, $\text{C}_{24}\text{H}_{17}\text{O}_6\text{N}$, from *p*-nitrobenzaldehyde and ethyl $\gamma\gamma$ -diphenylitaconate, crystallises in yellow prisms, melts and decomposes at 238° , and when oxidised yields benzophenone, *p*-nitrobenzaldehyde, and *p*-nitrobenzoic acid. The

sodium salt crystallises in yellow prisms; the *piperidine* salt forms nodular aggregates of slender, yellow needles and melts and decomposes at 181—182°.

α-p-Nitrophenyl-δδ-diphenylfulgide, $C_{24}H_{15}O_5N$, crystallises in orange, pleochroic, monoclinic plates melting at 228°, or from a mixture of benzene and chloroform in similar crystals melting at 224°. G. Y.

Butadiene Compounds. XIII. Aminotriphenylfulgenic Acid. HANS STOBBE and ALBERT KÜLLENBERG (*Ber.*, 1905, 38, 4087—4090).—The *α*-aminophenyl-δδ-diphenylfulgenic acids are formed by reducing the corresponding *α*-nitrophenyl acids with ferrous sulphate in ammoniacal solution and precipitating the product with the calculated quantity of *N*-hydrochloric acid.

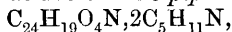
α-o-Aminophenyl-δδ-diphenylfulgenic acid,



is obtained as a yellow, amorphous mass, which melts and decomposes at 175—177° and is readily soluble in hydrochloric acid. The *piperidine* salt, $C_{24}H_{19}O_4N, 2C_5H_{11}N$, crystallises in yellow needles, melts and decomposes at 192—193°, and on treatment with aqueous silver nitrate forms the *silver* salt, $C_{24}H_{17}O_4NaAg_2$, as a white, flocculent precipitate which becomes yellow on drying.

α-m-Aminophenyl-δδ-diphenylfulgenic acid, $C_{24}H_{19}O_4N$, crystallises in yellow, monoclinic prisms, melts and decomposes at 224°, and when boiled with acetyl chloride forms *α-m-acetylaminophenyl-δδ-diphenyl-*

fulgide, $NHAc \cdot C_6H_4 \cdot CH:C(CO) \cdot C(CO) \cdot O$, which crystallises in slender, yellow needles and melts at 215°. The *piperidine* salt,



forms long, dirty-yellow needles and melts and decomposes at 177—178°.

α-p-Aminophenyl-δδ-diphenylfulgenic acid is amorphous; the *piperidine* salt forms large, dark yellow crystals and melts and decomposes at 182—183°; the *copper* salt, $C_{27}H_{17}O_4NCu$, is obtained as a light brown, amorphous precipitate. G. Y.

Resin Acids from Conifers. V. ALBERT VESTERBERG (*Ber.*, 1905, 38, 4125—4132. Compare *Abstr.*, 1886, 365, 1038; 1888, 294; 1904, i, 151; Ducommun, *Chem. Zeit.*, 1885, 1592).—Although *d*- and *l*-pimaric acids yield sparingly soluble, crystalline ammonium salts, a mixture of either acid with a large quantity of abietic acid produces a gelatinous salt. When the two acids are in the proportions 1:10, the salt remains gelatinous for weeks, but in the proportions 1:5 crystals are often observed in the course of a few days.

The separation of the pimaric acid is best accomplished by the following processes: (a) fractional crystallisation of the acids from 85 per cent. (vol.) alcohol until an acid is obtained which gives a crystalline ammonium salt; (b) repeated crystallisation of the sodium salt from water containing a small amount of sodium hydroxide; (c) crystallisation of the acid from alcohol or acetic acid.

d-Pimaric acid has been isolated by this method from French colophony and from the resin of *Pinus sylvestris*. J. J. S.

Positions of the NO_2 and NH_2 Groups in the Mononitro- and Amino-derivatives of Piperonylaldehyde and Piperonylic Acid. EFISIO MAMELI (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 424—432, 510—518).—The positions of the substituent nitrogen chains in the nitro- and amino-derivatives of piperonaldehyde and of the corresponding acid have not yet been absolutely proved (compare Abstr., 1904, i, 668, 743, and 1023; 1905, i, 203, 889). The following are the results of the author's investigations on this subject.

The oxidation of nitropiperonaldehyde yields the nitropiperonylic acid melting at 172° and already obtained by Jobst and Hesse by the nitration of piperonylic acid (Abstr., 1878, 733; 1880, 325). This nitro-acid or its calcium salt, when decomposed by heat, yields nitro-catechol methylene ether, which can also be obtained by distilling an alkaline solution of nitropiperonaldehyde in a current of steam. The nitro-groups in nitropiperonaldehyde and in nitrocatecholmethylene ether must have the same position relatively to the other substituents as that in nitropiperonylic acid. Reduction of the last-named compound gives rise to the *p*-aminocatechol methylene ether (6-amino-

3:4-methylenecatechol), $\text{CH}_2 \begin{smallmatrix} \text{O} \cdot \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{NH}_2 \\ \parallel \\ \text{O} \cdot \text{C} \cdot \text{CH} \cdot \text{CH} \end{smallmatrix}$, already prepared by

Rupe and von Majewski (Abstr., 1901, i, 103), by van Linge (Abstr., 1897, i, 618), and by Hesse (*loc. cit.*). The nitro-group in nitropiperonylic acid must therefore occupy the 6-position with reference to the carboxyl group, the $-\text{O} \cdot \text{CH}_2 \cdot \text{O}-$ group being in the 3:4-position. Confirmation of this conclusion has been obtained by preparing, from nitropiperonylaldehyde and from nitropiperonylic acid, the 4-nitro-1:2-dihydroxybenzene described by various authors.

The results given indicate that, when piperonaldehyde or piperonylic acid is nitrated directly, the first nitro-group introduced enters in the 6-position with respect to the aldehyde or carboxyl group in position 1, and the dioxymethylene complex in the position 3:4, and that further nitration gives rise to symmetrical tetra-substituted derivatives.

The above constitution for nitropiperonaldehyde has been confirmed in an indirect manner by the recent work of Herz (Abstr., 1905, i, 778). T. H. P.

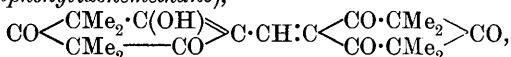
Tetramethylphloroglucinolaldehyde. JOSEF HERZIG and FRANZ WENZEL (*Monatsh.*, 1905, 26, 1359—1389. Compare Abstr., 1904, i, 251).—[With PETER RONA.]—Dimethylphloroglucinolaldehyde is heated with methyl iodide and potassium hydroxide in methyl-alcoholic solution in a reflux apparatus during one day, and after addition of further quantities of potassium hydroxide and methyl iodide again for one day. After distillation of the alcohol, the residue is treated with water and ether, when there are obtained an aqueous solution of the potassium derivative of tetramethylphloroglucinolaldehyde (1) and an ethereal solution of a condensation product (2).

(1) *Tetramethylphloroglucinolaldehyde*, $\begin{smallmatrix} \text{CMe}_2 \cdot \text{CO} \cdot \text{C} \cdot \text{CHO} \\ \parallel \\ \text{CO} \cdot \text{CMe}_2 \cdot \text{C} \cdot \text{OH} \end{smallmatrix}$, obtained

on acidification of the alkaline solution, crystallises from ether in large prisms or from methyl alcohol in colourless, rectangular plates, melts

at 70—71°, is readily soluble in benzene, but less soluble in methyl or ethyl alcohol, and dissolves in aqueous potassium hydroxide to form a colourless solution which remains unchanged on prolonged warming; it may be titrated with *N*/10 potassium hydroxide, using phenolphthalein as indicator. The *potassium* derivative, $\text{OK} \cdot \text{C}_6\text{O}_2\text{Me}_4 \cdot \text{COH}$, forms colourless crystals and is not decomposed by carbon dioxide in aqueous solution. The *oxime*, $\text{OH} \cdot \text{C}_6\text{O}_2\text{Me}_4 \cdot \text{CH} : \text{NOH}$, crystallises from ethyl acetate in white needles, commences to decompose at 189°, and melts at 196° to a dark yellow mass. When heated with acetic anhydride and sodium acetate at 160—180°, or when boiled with acetic anhydride only, tetramethylphloroglucinolaldehyde forms the *coumarin* derivative, $\text{C}_6\text{O}_2\text{Me}_4 \begin{smallmatrix} \text{CH} : \text{CH} \\ \text{O} \text{---} \text{CO} \end{smallmatrix}$, which crystallises from methyl alcohol and melts at 205—208°. The *methyl ether*, $\text{OMe} \cdot \text{C}_6\text{O}_2\text{Me}_4 \cdot \text{CHO}$, is formed by the action of diazomethane on tetramethylphloroglucinolaldehyde in ethereal solution; it crystallises from alcohol and melts at 100°. When oxidised with potassium permanganate in alkaline solution, the aldehyde yields a *substance* which crystallises in glistening scales, melts and evolves gas at 100°, and when heated with alcohol or benzene forms carbon dioxide and the condensation product melting at 210—212°.

[With WILHELM REISMANN.]—(2) The *condensation product* (6-hydroxy-2 : 2' : 4 : 4' : 6'-pentaketo-3 : 3 : 3' : 3' : 5 : 5 : 5' : 5'-octamethyltetrahydrophenylphenylidenemethane),



is obtained on evaporation of the ethereal solution and treatment of the residue with benzene; it is formed also together with formic acid when tetramethylphloroglucinolaldehyde is dissolved in dilute methyl alcohol, or is boiled with water, or when its potassium derivative is treated with methyl sulphate. After repeated recrystallisation from a mixture of chloroform and light petroleum, it forms nodular aggregates of white needles and melts at 217°; it does not yield an acetyl derivative when boiled with sodium acetate and acetic anhydride. The *methyl ether*, $\text{C}_{21}\text{H}_{25}\text{O}_5 \cdot \text{OMe}$, formed by the action of diazomethane on the condensation product in ethereal solution, separates from alcohol in colourless crystals, melts at 163—164°, and when treated with hydroxylamine hydrochloride in presence of sodium hydrogen carbonate or sodium methoxide yields a *product* which contains nitrogen and melts at 182°.

The condensation product dissolves in aqueous potassium hydroxide to form a yellow solution which becomes colourless, slowly at the laboratory temperature, quickly on evaporation, with formation of the potassium derivative of tetramethylphloroglucinolaldehyde and tetramethylphloroglucinol, melting at 192° (m. p. 187—188°; Reisch, Abstr., 1899, i, 803). The condensation product is again formed when the products of its hydrolysis are boiled with water containing a few drops of hydrochloric acid.

The action of methyl-alcoholic potash on the methyl ether of the condensation product leads to the hydrolysis of the methoxy-group,

and therefore to the formation of the same decomposition products as are obtained from the hydroxy-compound. When treated with concentrated sulphuric acid, the methyl ether yields the condensation product.

When reduced with zinc dust and aqueous potassium hydroxide, the condensation product forms a *dihydro*-derivative, $C_{21}H_{28}O_6$, which crystallises from benzene in slender needles and melts at 173° . It is formed also from tetramethylphloroglucinol by the action of (a) formaldehyde and concentrated sulphuric acid at 40° ; (b) of formaldehyde and potassium hydroxide in warm methyl-alcoholic solution; or (c) of boiling aqueous formaldehyde. The *methyl ether*, $C_{21}H_{26}O_4(OMe)_2$, formed by the action of diazomethane on the reduction product in ethereal solution, crystallises from methyl alcohol in stout needles, melts at 81° , and when boiled with hydriodic acid forms an *anhydride*, $C_{21}H_{26}O_5$, which is formed also by the action of concentrated sulphuric acid on the reduction product on the water-bath, or by boiling this with acetic anhydride and sodium acetate; it crystallises in needles and melts at 190° .

On prolonged action of potassium hydroxide and methyl iodide on dimethylphloroglucinolaldehyde, there is formed, in addition to tetramethylphloroglucinolaldehyde and its condensation product, a substance, $C_{22}H_{26}O_5$, which crystallises in glistening needles and melts at 173° .
G. Y.

Hydroxylamine Derivatives of Ketones of the Type $CO(CH:CHR)_2$. GAETANO MINUNNI and RICCARDO CIUSA (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 420—424. Compare Abstr., 1905, i, 245).—Attempts to determine the constitution of the base $C_{17}H_{18}N_2$, obtained by reducing α -dibenzylideneacetonehydroxylamineoxime (*loc. cit.*), by preparing its oxidation products have been unsuccessful. The compound, $C_{17}H_{16}N_2(OH)_2$, prepared by reducing disalicylideneacetonehydroxylamineoxime, gives mainly resinous products on oxidation, only a small quantity of a crystalline product being obtained by treatment with potassium permanganate and sulphuric acid.

Bromo- α -dibenzylideneacetonehydroxylamineoxime, $C_{17}H_{18}O_2N_2Br$, separates from alcohol in white crystals melting and decomposing at 172° and dissolves in methyl alcohol or chloroform and, to a slight extent, in ethyl acetate.

Oxidation of α -dibenzylideneacetonehydroxylamineoxime by means of amyl nitrite or acid potassium permanganate solution yields a small quantity of a *substance*, $C_{17}H_{14}ON_2$, separating from aqueous alcohol in yellow crystals which soften at 165° , melt and decompose at 176° , and are soluble in almost all the organic solvents.

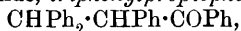
Reduction of β -dibenzylideneacetonehydroxylamineoxime by means of sodium in amyl alcohol solution, gives an oily base, the hydrochloride of which melts at 234° and the platinichloride at 268° ; the *benzoyl* derivative, $C_{17}H_{17}N_2Bz$, of the base crystallises from a mixture of ethyl acetate and alcohol in white needles which blacken at 260° , melt at 290° , and dissolve readily in methyl or ethyl alcohol and, to a less extent, in carbon tetrachloride.

Disalicylideneacetonehydroxylamineoxime, $C_{17}H_{16}O_2N_2(OH)_2$, crystal-

lises from alcohol in hard prisms melting and decomposing at 207° , and is slightly soluble in ether, benzene, ethyl acetate, or methyl alcohol; it dissolves in potassium hydroxide solution or in hydrochloric acid, and also in sulphuric acid, to which it imparts a blood-red coloration. Its *tetrabenzoyl* derivative, $C_{17}H_{14}O_4N_2Bz_4$, crystallises from alcohol in hard, minute prisms melting at 135° , and dissolves readily in methyl alcohol and, to a slight extent, in ether, benzene, or ethyl acetate. On reduction with sodium and amyl alcohol, it gives a *compound*, $C_{17}H_{16}N_2(OH)_2$, which crystallises from alcohol in white leaflets melting and decomposing at 191° and is soluble in ether or benzene with difficulty, in ethyl acetate with greater readiness, and in acetic, hydrochloric, or sulphuric acid or potassium hydroxide solution very readily.

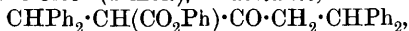
T. H. P.

Reaction between Organic Magnesium Compounds and Unsaturated Compounds. VII. Complex Products from Cinnamic Esters. ELMER P. KOHLER and GERTRUDE HERITAGE (*Amer. Chem. J.*, 1905, **34**, 568—580).—*Phenyl α -phenylcinnamate* crystallises in needles, melts at 142° , is sparingly soluble in alcohol or ether, moderately so in acetone or benzene, and readily in chloroform. When a solution of the ester in benzene is boiled with excess of magnesium phenyl bromide, *triphenylpropiophenone*,



is produced, which crystallises in small, colourless needles, melts at 182° , is readily soluble in chloroform, moderately so in benzene or hot acetone, and very slightly in alcohol or ether; it yields neither a hydrazone nor an oxime.

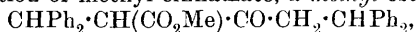
When phenyl cinnamate (1 mol.) is added to a well-cooled ethereal solution of magnesium phenyl bromide (3 mols.) and the product is decomposed with cold hydrochloric acid, diphenylpropionic acid and diphenylpropiophenone are produced together with a small quantity of diphenyl. If the solution of the bromide (1 mol.) is slowly added to a cold solution of the ester (1 mol.), a *substance*,



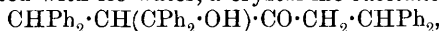
is produced which crystallises in long needles, melts at 180 — 182° , is readily soluble in chloroform or benzene, moderately in ethyl acetate or hot acetone, and very slightly in alcohol or ether; it is easily hydrolysed by potassium hydroxide with formation of potassium phenoxide, potassium carbonate, and *aa $\epsilon\epsilon$ -tetraphenylpentane- γ -one*, $CO(CH_2 \cdot CHPh_2)_2$, which crystallises in colourless needles, melts at 130° , is readily soluble in ethyl acetate or chloroform, and moderately so in alcohol or acetone, does not combine with bromine, and is not attacked by potassium permanganate. Tetraphenylpentanone *oxime* crystallises in needles, melts at 115 — 116° , and when treated with phosphorus pentachloride is converted into the isomeric *acid anilide*, which forms small, lustrous prisms, melts at 155° , and if heated in a sealed tube with strong hydrochloric acid yields $\beta\beta$ -diphenylpropionic acid and $\beta\beta$ -diphenylethylamine.

In an earlier paper (Abstr., 1905, i, 208), the effect of adding methyl cinnamate to an excess of magnesium phenyl bromide was described.

If, on the other hand, the magnesium compound is added slowly to a well-cooled solution of methyl cinnamate, a *methyl ester*,



corresponding with the phenyl ester obtained from phenyl cinnamate under the same conditions, is produced, which crystallises in slender needles, melts at 211—213°, is readily soluble in chloroform or benzene, moderately in acetone, and very slightly so in alcohol or ether; when heated at 200° with concentrated hydrochloric acid, it is decomposed with formation of 2 mols. of $\beta\beta$ -diphenylpropionic acid. β -Benzoyl- $\alpha\alpha\alpha$ -tetraphenylpentane- γ -one, $\text{CHPh}_2 \cdot \text{CHBz} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CHPh}_2$, which is obtained as a by-product in the preparation of the methyl ester just described, and can be prepared by dropping methyl cinnamate into a boiling solution of magnesium phenyl bromide, crystallises in needles, melts at 166°, is readily soluble in chloroform or acetone, moderately in alcohol, and sparingly so in ether. This ketone is hydrolysed by boiling alcoholic potassium hydroxide with formation of tetraphenylpentanone and potassium benzoate, whilst aqueous potassium hydroxide converts it into diphenylpropiophenone and potassium diphenylpropionate. If ethereal solutions of methyl cinnamate and magnesium phenyl bromide are boiled together for three or four hours and the product is treated with ice-water, a crystalline *substance*,



is obtained, which melts at 153°, is readily soluble in acetone or chloroform, and moderately so in alcohol, and when heated alone at 270—300°, or with concentrated hydrochloric acid at 200°, is converted into benzophenone and tetraphenylpentanone. E. G.

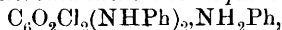
Soluble Preparations of *o*-Nitrophenyl- β -lactomethylketone.

FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 160783).—*o*-Nitrophenyl- β -lactomethylketone is useful for the production of indigo-blue on the fibre, but is very sparingly soluble. It dissolves, however, in aqueous solutions of the alkali salts of benzylaniline-sulphonic acid, $\text{CH}_2\text{Ph} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$, 2 mols. of the ketone requiring at least 1 mol. of the acid for solution. Salts of benzyltoluidinesulphonic acids or of chlorobenzylanilinesulphonic acids, and homologues of the ketone, show a similar behaviour. C. H. D.

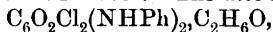
Derivatives of Tetrachloro-*o*-benzoquinone. C. LORING JACKSON and R. D. MAC LAURIN (*Ber.*, 1905, 38, 4103—4105).—

Hexachloro-o-quinocatechol ether, $\text{C}_6\text{O}_2\text{Cl}_2 \langle \text{O} \rangle \text{C}_6\text{Cl}_4$, prepared by the action of tetrachlorocatechol on tetrachloro-*o*-benzoquinone dissolved in dilute acetic acid, separates from benzene in deep red crystals, melts at 300°, and is more soluble than the bromo-compound (Jackson and Koch, *Abstr.*, 1901, i, 597). It is reduced by sodium amalgam to

hexachlorodihydroxycatechol ether, $\text{C}_6\text{Cl}_2(\text{OH})_2 \langle \text{O} \rangle \text{C}_6\text{Cl}_4$, which crystallises from alcohol in colourless needles and melts at 290°. When condensed with aniline, tetrachloro-*o*-benzoquinone yields a double compound, *aniline-dichlorodianilino-o-benzoquinone*,



which crystallises from benzene in long, thin, brown needles and melts and decomposes at 164—165°. The *alcohol* compound,

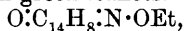


crystallises from alcohol in glistening, yellow plates and melts at 140—141°. *Dichlorodianilino-o-benzoquinone*, $\text{C}_6\text{O}_2\text{Cl}_2(\text{NHPh})_2$, prepared by crystallising the aniline compound from a mixture of benzene and light petroleum, separates in reddish-purple, pointed needles and melts at 194—195°. *Chlorodianilino-p-quinoneanil*,



prepared by the action of alcohol and aniline on the preceding compound, crystallises from benzene and alcohol in broad, black, glistening needles and melts at 180°. T. M. L.

1:2-Anthraquinone. KASIMIR LAGODZINSKI (*Annalen*, 1905, **342**, 59—89. Compare Abstr., 1904, i, 158).—1-Nitroso-2-anthrol, which the author regards as being in the tautomeric form, $\text{O}:\text{C}_{14}\text{H}_8:\text{N}\cdot\text{OH}$, can be prepared from 2-anthrol in alcoholic solution by treatment, successively, with an aqueous solution of zinc chloride and sodium nitrite; the mixture is slowly heated and the zinc salt of the nitroso-anthrol separates; it crystallises in orange needles decomposing at 188°, and gives an indigo-blue coloration with concentrated sulphuric acid. The *potassium* derivative, $\text{C}_{14}\text{H}_8\text{O}_2\text{NK}$, forms green and the *sodium* derivative yellowish-green leaflets. The *ethyl ether*,



prepared from the silver salt and ethyl iodide, crystallises in golden-yellow leaflets melting at 143°. The *methyl ether* crystallises in similar forms, melting at 129—130°.

1-Amino-2-anthrol, $\text{NH}_2\cdot\text{C}_{14}\text{H}_8\cdot\text{OH}$, is obtained by reducing either the nitrosoanthrol with stannous chloride and hydrochloric acid or with hydrogen sulphide in alkaline solution, or benzeneazo-2-anthrol with zinc dust and hydrochloric acid; it crystallises in yellowish-green leaflets decomposing at 140—150°; the *hydrochloride* and the *sulphate* form greenish-yellow needles; when heated with concentrated sulphuric acid, a blood-red coloration is obtained. A *triacyl* derivative, $\text{N}(\text{Ac})_3\cdot\text{C}_{14}\text{H}_8\cdot\text{OAc}$, crystallises in greenish-grey leaflets melting at 165°, and dissolves in alcohol solution with a blue fluorescence; on hydrolysis with dilute alcoholic potassium hydroxide, 1-acetyl-amino-2-anthrol is obtained as green leaflets decomposing at 200—220°; its alcoholic solution has a bluish-green fluorescence.

1:2-Anthraquinone, $\text{C}_{14}\text{H}_8\text{O}_2$, is formed when the salts of amino-anthrol are oxidised in the cold with ferric chloride or chromic acid; it crystallises in orange-yellow needles melting and decomposing at 185—190°, and dissolves in sulphuric acid with a bluish-violet coloration. It condenses with *o*-phenylenediamine, yielding 1:2-

anthraphenazine, $\text{C}_{14}\text{H}_8\langle\text{N}\rangle\text{C}_6\text{H}_4$, which crystallises in dark yellow

leaflets melting at 221—222°; the *hydrochloride* is cherry-red and the *sulphate* bluish-green. When oxidised with chromic acid in acetic acid solution, triacetylaminanthrol yields 1-diacetyl-amino-2-acetoxy-anthraquinone, $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{C}_6\text{H}_2(\text{OAc})\cdot\text{N}(\text{Ac})_2$, which crystallises in pale

yellow needles melting at 189° . On hydrolysis, it is converted into 1-amino-2-hydroxyanthraquinone, crystallising in dark red needles melting at 250 — 251° and identical with Liebermann's α -alizarinamide. Alizarin is produced by heating the substance last mentioned under pressure with hydrochloric acid at 250° ; the transformation is not produced by diazotisation.

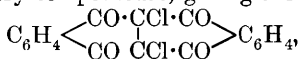
1:2-Anthraquinol (*loc. cit.*), prepared from the quinone, crystallises in greenish-yellow leaflets melting and decomposing at 131° ; the alkaline solution is at first cherry-red, but soon blackens on oxidation. The *diacetyl* derivative forms yellow aggregates melting at 145° , and by oxidation with chromic acid is converted into diacetylalizarin.

K. J. P. O.

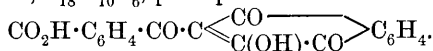
Chlorination of Mono- and Di-amino-derivatives of Anthraquinone. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 158951. Compare Wohl, this vol., i, 9).—The mono- and di-amino-derivatives of anthraquinone are readily chlorinated by means of sulphuryl chloride. Thus, β -aminoanthraquinone yields a monochloro-derivative, 1:5-diaminoanthraquinone yields a tetrachloro-derivative, crystallising from nitrobenzene in glistening, brown needles, and 2:6-diaminoanthraquinone yields a dichloro-derivative. The solubilities of many such chloro-compounds in sulphuric acid and in organic solvents are described.

C. H. D.

Studies in the Naphthacene Series. HUGO VOSWINCKEL (*Ber.*, 1905, 38, 4015—4021).—Naphthacenediquinone (Gabriel and Leupold, *Abstr.*, 1898, i, 482) dissolved in glacial acetic acid is attacked by chlorine at the ordinary temperature, giving the *dichloride*,

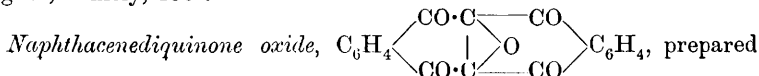


which crystallises from nitrobenzene in rhombic crystals and melts at 175° ; with reducing agents it gives dihydroxynaphthacenequinone (Gabriel and Leupold, *loc. cit.*), and on warming with dilute aqueous sodium hydroxide the same substance is also formed, but the principal product is an *acid*, $\text{C}_{18}\text{H}_{10}\text{O}_6$, perhaps



This crystallises from dilute alcohol containing hydrochloric acid in bright yellow, transparent prisms, melts at 185° , and gives a hydrazone and a red, crystalline *silver salt*, $\text{C}_{18}\text{H}_5\text{O}_6\text{Ag}_2\text{H}_2\text{O}$.

With bromine in glacial acetic acid, naphthacenediquinone gives *trihydroxynaphthacenequinone bromide*, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \cdot \text{C} = \text{C}(\text{OH}) \\ | \quad | \\ \text{CO} \cdot \text{CBr} \cdot \text{C}(\text{OH})_2 \end{array} \text{C}_6\text{H}_4$, which separates in well-formed, colourless prisms and melts at 198° ; a little dihydroxynaphthacenequinone is also formed. When the bromide is shaken with aqueous sodium hydroxide, it seems to yield the acid, $\text{C}_{18}\text{H}_{10}\text{O}_6$, described above, but the melting point is slightly higher, namely, 199° .



by leaving powdered naphthacenediquinone with an aqueous suspension of bleaching powder for several days, crystallises from benzene in small, orange-coloured needles, melts and decomposes at about 240° , and is easily reduced to dihydroxynaphthacenequinone; with aqueous sodium hydroxide, the acid, $C_{18}H_{10}O_6$, is obtained, melting at 199° .

W. A. D.

Preparation of Bornylenediamine. PAUL DUDEN (D.R.-P. 160103).—Bornylenediamine (camphanediamine) is prepared by reducing amino-, isonitroso-, or isonitro-camphoroxime by means of sodium and alcohol, sodium amalgam, or electrolytic hydrogen. *Bornylenediamine* forms a waxy solid, boils at 246° , and dissolves with extreme readiness in water. The *diacetyl* derivative occurs in two stereoisomeric modifications, melting at 246° and 253° respectively.

C. H. D.

Chemical Investigation of Resin from the Pine (*Pinus abies*). PETER KLASON and JOHN KÖHLER (*Arkiv Kem. Min. Geol.*, 1905, 2, i, No. 3, 1—39).—Resin from the pine contains two isomorphous acids, α - and β -colophonic acids, $C_{20}H_{30}O_2$. The acids have the normal molecular weight in freezing acetic acid and give the acid value 185.4. The separate acids have not been obtained absolutely pure, so that the physical constants given below are only approximately correct.

α -Colophonic acid crystallises from alcohol in colourless, oblique, monoclinic prisms [$a:b:c = 1.1282:1:0.9716$; $\beta = 71^{\circ}24'$], melts at 177 — 182° , and has $[\alpha]_D - 59.41^{\circ}$.

β -Colophonic acid separates in less well-developed crystals than the α -acid, melts at 168 — 173° , and has $[\alpha]_D + 52.2^{\circ}$.

The *ammonium*, $NH_3 \cdot 2C_{20}H_{30}O_2$, *calcium*, $Ca(C_{20}H_{29}O_2)_2$, and *barium*, $Ba(C_{10}H_{29}O_2)_2 \cdot 2H_2O$, salts of the mixed acids were prepared.

T. H. P.

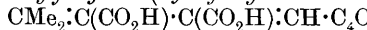
Gutta Percha and Balata. WILLIAM A. CASPARI (*J. Soc. Chem. Ind.*, 1905, 24, 1274—1278).—Analyses of various guttas and balata, purified by solution in benzene and precipitation with alcohol thrice repeated, confirmed the formula $(C_5H_8)_n$. Pure gutta is of a leathery consistence and almost destitute of elasticity; below 100° , it becomes soft and can be kneaded, whilst caoutchouc becomes sticky and moderately plastic, but retains some resilience; at higher temperatures, the two hydrocarbons tend to approximate in behaviour. When dissolved in dry carbon tetrachloride and treated with chlorine, the hydrocarbons of gutta, caoutchouc, or balata yielded substances the composition of which approximated to the formula $C_{20}H_{36}Cl_{14}$; the substances, when purified by precipitation from dilute benzene or chloroform solution by means of alcohol and dried in a vacuum, presented white, toughish plates. Substances prepared similarly by the action of bromine gave analytical numbers leading to the formula $C_{50}H_{46}Br_{10}$; iodine in chloroform solution yielded substances containing between 12.11 and 13.47 per cent. of iodine. Benzene solutions of gutta or balata saturated with dry hydrogen chloride and

precipitated with alcohol gave substances which, when redissolved and again precipitated, formed white, leathery flakes, easily soluble in benzene or in chloroform, and had the composition $C_{30}H_{45} \cdot 5HCl$; the behaviour of caoutchouc was found to be somewhat different. A solution of nitrogen peroxide and oxygen in benzene, added to a benzene solution of the hydrocarbons, produced green, gelatinous precipitates of variable composition; on adding more nitrogen peroxide, yellow clots separated, which had the composition $C_{10}H_{16}O_4N_2$; on subjecting these substances to the protracted action of nitrogen peroxide, they produced substances which, when pure, were saffron-yellow powders which dissolved in acetone, ethyl acetate, alkalis, and ammonia with a deep orange colour; their composition is represented by the formula $C_{10}H_{15}O_7N_3$. By the action of nitric acid, a substance of the formula $C_{15}H_{21}O_{11}N_4$ was obtained. Benzene solutions of the hydrocarbons on treatment with dry nitric oxide gave substances the composition of which is represented by the formula $C_{10}H_{16}O_2N$. The conclusion is drawn from these experiments that the hydrocarbons of gutta percha and of balata are identical, whilst as regards gutta and caoutchoucs it seems as if these were a common molecule, differences in the aggregation of which caused differences in mechanical structure.

P. H.

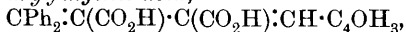
Butadiene Compounds. XI. Parallel Coloured Furyl- and Phenyl-fulgides. HANS STOBBE and RICHARD ECKERT (*Ber.*, 1905, **38**, 4075—4081).—The furyl group has stronger chromophoric properties than has the phenyl group; a number of furyl and the corresponding phenyl compounds are quoted to show that where these have the same colour, the former have the deeper shade. This is the case in the fulgide series, the three furyl-fulgides described below being light orange, dichromate-red, and reddish-brown, whilst the corresponding phenyl compounds are light yellow, orange-red, and lemon-yellow respectively (*Abstr.*, 1905, i, 857; this vol., i, 22).

α -Furyl- $\delta\delta$ -dimethylfulgenic (α -furfurylideneteraconic) acid,



formed by the action of sodium ethoxide on ethyl dimethylitaconate and furfuraldehyde in absolute alcoholic solution, separates from 20 per cent. acetic acid in small, slightly yellow, rhombic crystals, softens at 204° , and melts and decomposes at 218° . When treated with acetyl chloride, cooled by a freezing mixture, it yields *α -furyl- $\delta\delta$ -dimethylfulgide*, $C_{19}H_{10}O_4$, which crystallises from light petroleum in small, light orange, monoclinic prisms, melts at 63° , is readily soluble in ether, chloroform, benzene, or carbon disulphide, and dissolves in concentrated sulphuric acid to form a yellow solution, which becomes greenish-brown, and finally reddish-brown, changing to yellow on dilution with water.

$\delta\delta$ -Diphenyl- α -furylfulgenic acid,

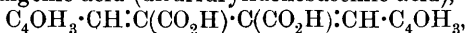


formed from furfuraldehyde and ethyl diphenylitaconate in alcoholic sodium ethoxide solution, crystallises from benzene in shimmering, yellow leaflets containing C_6H_6 , which is lost at 100° , becomes dark at 187° , and melts and decomposes at 202° . The *sodium salt*,

$C_{22}H_{14}O_5Na, 2H_2O, 2C_2H_6O$, crystallises from 70 per cent. alcohol in white plates.

$\delta\delta$ -Diphenyl- α -furylfulgide, $C_{22}H_{14}O_4$, formed by pouring cold acetyl chloride on to the dicarboxylic acid, crystallises from carbon disulphide in dark red prisms, which lose CS_2 on exposure to air; when free from carbon disulphide, it is dichromate-red, melts at 156° , is easily soluble in chloroform or benzene, and dissolves in concentrated sulphuric acid to form a green solution which becomes brown, and on dilution with water deposits a greenish-blue, flocculent precipitate.

$\alpha\delta$ -Difurylfulgenic acid (difurfurylidenesuccinic acid),



is obtained by treating a mixture of 3 mols. of furfuraldehyde and 1 mol. of ethyl succinate in alcoholic solution with 2 mols. of sodium ethoxide in a yield of 15 per cent. of the theoretical; it melts at $227-228^\circ$ ($217-225^\circ$: Fichter and Scheuermann, Abstr., 1901, i, 479; $185-187^\circ$: Titherley and Spencer, Trans., 1904, 85, 190).

$\alpha\delta$ -Difurylfulgide (difurfurylidenesuccinic anhydride) forms brownish-red, rhombic crystals, softens at 197° , and melts at 204° (187° : Titherley and Spencer, *loc. cit.*, p. 188). G. Y.

Diphenyl-*o*-phenoxylenedihydroanthracene. FRITZ ULLMANN and JACOB TSCHERNIAK (*Ber.*, 1905, 38, 4110—4111).—2'-Hydrofluoranyldiphenylcarbinol, $O \langle \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} \rangle CH \cdot C_6H_4 \cdot CPh_2 \cdot OH$, prepared by the action of bromobenzene and magnesium on methyl hydrofluoranate (Meyer, Abstr., 1895, i, 291), $O \langle \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} \rangle CH \cdot C_6H_4 \cdot CO_2Me$, separates from benzene in colourless crystals and melts at 196° . By the action of acetic and sulphuric acids, it is converted into 10:10-diphenyl-1:9-*o*-phenoxylenedihydroanthracene, $\begin{smallmatrix} C_6H_4 \cdot CH - C_6H_4 \\ | \qquad \qquad | \\ CPh_2 \cdot C_6H_3 \cdot O \end{smallmatrix}$, which separates in colourless crystals and melts at 325° . T. M. L.

Salts of the Alkaloid Cinchonamine. BERNARD F. HOWARD and F. PERRY (*J. Soc. Chem. Ind.*, 1905, 24, 1281—1283).—The cinchonamine used in the investigation was obtained from a sample of the crude nitrate which had been precipitated from the alkaloid of the bark of *Remijia Purdeiana*. The crude salt was twice recrystallised from water and converted into the hydrochloride, in which form it was several times recrystallised; on precipitating the base and recrystallising it from acetone, it was obtained as a perfectly white, crystalline product. Cinchonamine hydrochloride, $C_{19}H_{24}ON_2 \cdot HCl$, crystallises from the acid solution in soft, almost white, glistening laminae. A hot saturated neutral solution of the hydrochloride cooled to 27° deposits cubical crystals of a monohydrated salt. A dihydrochloride could not be obtained. The hydrobromide was prepared in a manner exactly similar to the hydrochloride and was found to be anhydrous; it is very slightly soluble in cold water. The hydriodide prepared by double decomposition of a salt of cinchonamine with potassium iodide or by boiling the alkaloid with 5 per cent. hydriodic acid crystallises in shining, slightly yellow plates; on exposure to dry air, it loses hydro-

gen iodide ; it is almost insoluble in cold water, but is fairly soluble at higher temperatures. The platinichloride forms a very insoluble, semicrystalline, yellow solid. The *salicylate* prepared by neutralising a warm solution of salicylic acid with cinchonamine forms a resinous mass which crystallises from dilute aqueous solutions in thick, colourless prisms, which are very readily soluble in acetone. The sulphate was obtained by neutralising an alcoholic solution of the alkaloid with dilute sulphuric acid at a temperature just below the boiling point of alcohol ; on rendering the neutral solution just acid and cooling, it was deposited in small needles ; it is extremely soluble in water and is practically insoluble in absolute alcohol ; it is very soluble in pyridine and crystallises from it with one molecule of the solvent. The acid sulphate, $C_{19}H_{24}ON_2 \cdot H_2SO_4$, is best prepared by dissolving the sulphate in a small quantity of water at the temperature of the boiling water-bath and stirring in a molecular quantity of dilute sulphuric acid ; on slow evaporation in a vacuum, the solution deposits large, truncated octahedra. The *picrate* obtained as a yellow, amorphous powder by adding a cold aqueous solution of picric acid to the hydrochloride melts at 54° and contains $\frac{1}{2}H_2O$. Solubility curves are given for the haloid salts. P. H.

Nicotine and its Specific Rotation. I. FLORIAN RATZ. (*Monatsh.*, 1905, **26**, 1241—1252).—The author has purified two samples of nicotine of different origins by fractional distillation under 20 mm. pressure, and obtained two fractions, having $[\alpha]_D - 163.19^\circ$ and -166.77° at 20° respectively. The specific rotation of these fractions was not altered by further fractional distillation, but on conversion of each into the zincochloride, fractional crystallisation of this, and liberation and fractional distillation of the base, two specimens of pure nicotine were obtained. This boils at 246.2° under 719.8 mm. pressure, and has the sp. gr. 1.00924—1.00925 at $20^\circ/4^\circ$ and $[\alpha]_D - 169.22^\circ$ to -169.54° at 20° .

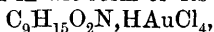
Nicotine zincochloride, $C_{10}H_{14}N_2 \cdot 2HCl \cdot ZnCl_2 \cdot H_2O$, is soluble in two parts of water, or 4—4.5 parts of 60 per cent. alcohol, or in 0.1 or 0.35 part of the boiling solvents respectively.

A table is given showing the sp. gr. and the specific rotation of nicotine as found by a number of authors. The different figures obtained previously must be due to the presence, in varying amounts, of an impurity which is removed only partly by fractional distillation ; the nature of this the author proposes to investigate. G. Y.

Scopolamine and Scopoline. ERNST SCHMIDT (*Arch. Pharm.*, 1905, **243**, 559—583. Compare *Abstr.*, 1892, 1255 ; 1895, i, 158 ; 1898, i, 499 ; 1903, i, 51).—Numerous attempts to obtain reactions which would correspond with the presence of ketonic oxygen in scopoline, $C_8H_{13}O_2N$, gave no positive result. Further, it was not found possible to reduce scopoline in either acid, neutral, or alkaline solution ; neither could a compound with hydrocyanic acid be obtained ; nor was a benzylidene derivative formed when scopoline and benzaldehyde were allowed to remain in acetic acid solution saturated with hydrogen

chloride, as happens with substances which contain a $\text{CH}_2\cdot\text{CO}$ group (Willstätter, Abstr., 1898, i, 160).

By methylating scopoline (Luboldt, Abstr., 1898, i, 499), a small quantity was obtained of a crystalline *methylscopoline* which melted at $69\text{--}70^\circ$; it was analysed in the form of its *aurichloride*,



which melts at 154° .

When scopoline is allowed to remain with hydrogen peroxide, it yields a product which melts and decomposes at 122° and forms a crystalline *hydrochloride*, $\text{C}_8\text{H}_{13}\text{O}_3\text{N}, \text{HCl}$; probably this product is an *oxide*, the NMe group having been converted into NMeO. Scopoline is oxidised but very slowly by a boiling solution of chromic and sulphuric acids; the products are scopoligenine, $\text{C}_7\text{H}_{11}\text{O}_2\text{N}$, pyridine methosulphate, methylamine, and carbon dioxide.

[With RUDOLF GAZE.]—Bromine, either in chloroform solution or in the form of vapour, converts scopoline partially into scopoligenine; in the latter case, a small quantity was also obtained of a substance melting at $110\text{--}113^\circ$, probably a *bromo-derivative* of scopoline.

Scopoligenine yields unsaturated hydrocarbons and pyridine when it is heated with zinc dust in a current of hydrogen gas.

When hydrobromoscopoline hydrobromide is boiled with phosphorus tribromide and the product reduced with zinc and dilute sulphuric acid, hydroscopolidine is formed; this was analysed in the form of its *aurichloride*, $\text{C}_8\text{H}_{15}\text{N}, \text{HAuCl}_4$, which melts at $204\text{--}206^\circ$.

Hydriodoscopoline hydriodide melts at 196° . The *aurichloride* of *hydroscopoline*, $\text{C}_8\text{H}_{15}\text{O}_2\text{N}, \text{HAuCl}_4$, which is obtained by reducing hydrobromoscopoline (Abstr., 1903, i, 51), melts at $200\text{--}201^\circ$.

New varieties of the platinichloride and aurichloride of scopoline, respectively anhydrous and with H_2O , are described; these melt practically at the same temperature as the salts known already. C. F. B.

Modern Theories of Double Linkings and the Constitutional Formula of Pyrrole. GIACOMO CIAMICIAN (*Gazzetta*, 1905, 35, ii, 384—393).—The author discusses the various formulæ which have been proposed for pyrrole, in which, as he has already pointed out (Abstr., 1893, i, 602), two valencies of the nitrogen atom exist in a latent condition. On the basis of Thiele's theory of partial valencies, he supposes that in thiophen, pyrrole, and furan the partial valencies of the group $-\text{CH}:\text{CH}:\text{CH}:\text{CH}-$ are more or less satisfied by the latent valencies of the sulphur, nitrogen, and oxygen respectively, the extent of this neutralisation being greatest with sulphur and least with oxygen (see also Abstr., 1905, i, 80). T. H. P.

Compounds of Copper Salts with Pyridine and Quinoline. PAUL PFEIFFER and V. PIMMER (*Zeit. anorg. Chem.*, 1905, 48, 98—111).—The following additive compounds of copper nitrate and pyridine have been prepared. $\text{Cu}(\text{NO}_3)_2, 2\text{C}_5\text{H}_5\text{N}$, a light blue powder; $\text{Cu}(\text{NO}_3)_2, 3\text{C}_5\text{H}_5\text{N}$, azure-blue crystals; $\text{Cu}(\text{NO}_3)_2, 4\text{C}_5\text{H}_5\text{N}$, violet plates; $\text{Cu}(\text{NO}_3)_2, 6\text{C}_5\text{H}_5\text{N}$, small, cobalt-blue crystals. The tetra-pyridine compound is readily formed from its components; with excess of the base, it forms the hexapyridine compound, whereas it yields the

di- and tri-pyridine compounds when heated carefully. The compounds $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{C}_5\text{H}_5\text{N} \cdot 2\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{C}_5\text{H}_5\text{N} \cdot 3\text{H}_2\text{O}$ have also been prepared; the former occurs in light blue plates, whilst the latter has a violet-blue colour.

Diquinoline cupric nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{C}_9\text{H}_7\text{N}$, prepared directly from its components, crystallises in transparent, indigo-blue needles.

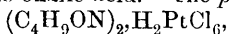
Dipyridine cupric bromide, $\text{CuBr}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$, prepared from its components, occurs in green needles; with excess of the base, it yields *hexapyridine cupric bromide*, $\text{CuBr}_2 \cdot 6\text{C}_5\text{H}_5\text{N}$, as a blue, crystalline mass. *Pyridinium cupric bromide*, $\text{Cu}(\text{C}_5\text{H}_6\text{N})_2\text{Br}_4$, prepared by dissolving the dipyridine additive compound in hydrobromic acid, forms lustrous, reddish-black, prismatic crystals; the corresponding quinolinium compound, $\text{Cu}(\text{C}_9\text{H}_8\text{N})_2\text{Br}_4 \cdot 3\text{H}_2\text{O}$, prepared by a similar method, crystallises in black plates.

G. S.

Aminoacetals and Aminoaldehydes. II. ALFRED WOHL (*Ber.*, 1905, **38**, 4154—4157. Compare Abstr., 1901, i, 513).—A summary of the results contained in the three following abstracts. Aminoaldehydes and their substitution derivatives are best purified in the form of their platinichlorides; the free aldehydes very readily undergo condensation, and in only a few cases have they been obtained pure by reducing to a minimum the decomposing action of heat, alkali, and water.

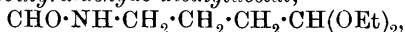
C. S.

γ -Aminobutyraldehyde and Pyrrolidine. ALFRED WOHL, KURT SCHÄFER, and A. THIELE (*Ber.*, 1905, **38**, 4157—4161).— γ -Aminobutyraldehyde diethylacetal is conveniently obtained by the interaction of β -chloropropaldehyde diethylacetal, sodium ethoxide, and dry hydrogen cyanide in alcoholic solution at 118—122° for two days, the product being subsequently reduced with sodium and absolute alcohol. *γ -Aminobutyraldehyde*, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHO}$, obtained by the decomposition of the acetal by a dilute solution of oxalic acid, forms a syrup which still contains oxalic acid. The *platinichloride*,



is an unstable, crystalline substance.

γ -Formylaminobutyraldehyde diethylacetal,



prepared from ethyl formate and the acetal base, boils at 170° under 14 mm. pressure and is soluble in water or the usual organic solvents.

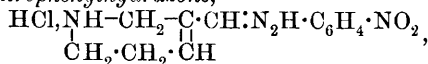
γ -Formylaminobutyraldehyde, $\text{CHO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHO}$, is obtained in an impure state by the decomposition of the acetal with oxalic acid. The *platinichloride*, $(\text{C}_5\text{H}_9\text{O}_2\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$, melts and decomposes at 176°.

1-Benzenesulphonyl-2-ethoxypyrrolidine, $\text{SO}_2\text{Ph} \cdot \text{N} \langle \text{CH}(\text{OEt}) \rangle \text{CH}_2$,

obtained by the action of benzenesulphonic chloride on an aqueous-alcoholic solution of γ -aminobutyraldehyde diethylacetal and treatment of the oil so produced with a 5 per cent. alcoholic potash, is a crystalline substance which melts at 76—78° and distils without decomposition. It is insoluble in water, but dissolves in ordinary organic solvents; it is reduced to pyrrolidine by sodium and hot amyl alcohol.

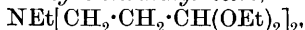
C. S.

Hydrogenated Pyridine-aldehydes. ALFRED WOHL, W. HERTZBERG, and M. S. LOSANITSCH (*Ber.*, 1905, **38**, 4161—4169).— β -*Imino-dipropaldehyde tetraethylacetal*, $\text{NH}[\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2]_2$, obtained by heating under pressure β -chloropropaldehyde diethylacetal (1 part) with a cold saturated solution of ammonia in alcohol (6 parts) at 118—120° for not more than nine hours, is a colourless, viscous liquid inclining to yellow; it boils at 157° under 15 mm. pressure, has a basic odour, is somewhat soluble in water, dissolves in the ordinary organic solvents, and has a sp. gr. 0.9466 at 15°. Dilute oxalic, hydrochloric, or sulphuric acid hydrolyses it to the extent of 88 per cent. Cold concentrated hydrochloric acid causes the formation of a syrup which was identified as Δ^3 -*tetrahydropyridine-3-aldehyde* in the form of the *hydrochloride* of its *nitrophenyllhydrazone*,



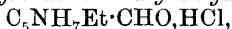
a hygroscopic, reddish-yellow substance which sinters at 173.5° and melts with decomposition at 251°.

β -*Ethyliminodipropaldehyde tetraethylacetal*,



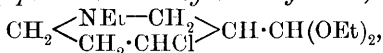
obtained from ethylamine and β -chloropropaldehyde diethylacetal in benzene solution at 135—140°, is a colourless, viscous oil which boils at 159° under 13 mm. pressure; it is sparingly soluble in water and is miscible with the ordinary organic solvents. The *platinichloride*, $(\text{C}_{16}\text{H}_{36}\text{O}_4\text{N})_2\cdot\text{H}_2\text{PtCl}_6$, separates from dilute alcohol in yellow, octahedral crystals which melt and decompose at 92—93° (corr.).

1-*Ethyl- Δ^3 -tetrahydropyridine-3-aldehyde hydrochloride*,



is obtained from the acetal by the action of cold concentrated hydrochloric acid. It separates from dilute alcohol in long, colourless crystals which melt at 208° (corr.), shows reducing properties, and gives a reddish-brown coloration with concentrated sulphuric acid and phenol or β -naphthol. The *platinichloride* forms yellow cubes which melt and decompose at 190°. The *hydrochloride* of the *nitrophenyllhydrazone* separates from dilute alcohol in reddish-yellow, hygroscopic needles which melt and decompose at 263°. The *hydrochloride* of the *oxime* forms long, colourless needles which melt at 248—249° (corr.). The free *oxime*, which is not produced by mixing its components, is obtained from the hydrochloride by the action of potassium carbonate; it crystallises in white scales and melts at 134° (corr.). The *acetate* of the *oxime*, obtained by the action of acetic anhydride and sodium acetate on the hydrochloride, boils at 102—105° under 0.1 mm. pressure. Thionyl chloride converts the hydrochloride of the *oxime* into the *hydrochloride* of the *nitrile*, $\text{C}_5\text{NH}_7\cdot\text{Et}\cdot\text{CN}\cdot\text{HCl}$, which separates from dilute alcohol in white needles melting at 265—266° (corr.).

4-*Chloro-1-ethylpiperidine-3-aldehyde diethylacetal*,



prepared by the action of hydrogen chloride on the hydrochloride of 1-ethyl- Δ^3 -tetrahydropyridine-3-aldehyde dissolved in absolute alcohol, is a colourless oil which boils at 79—80° under 0.05 mm. pressure. Its

reduction by sodium and absolute alcohol produces 1-ethylpiperidine-3-aldehyde diethylacetal, which is a colourless oil boiling at 63–65° under 0.04 mm. pressure.

C. S.

Free Aminoaldehydes. ALFRED WOHL and M. S. LOSANITSCH (*Ber.*, 1905, 38, 4170–4172).—1-Ethyl- Δ^3 -tetrahydropyridine-3-aldehyde, obtained from its hydrochloride (see preceding abstract) by the action of solid potassium carbonate, is a colourless, oily liquid with a basic stupefying odour; it boils at 52–54° under 0.06 mm. pressure, has an alkaline reaction and reducing properties, and is resinified by potassium hydroxide.

1-Ethylpiperidine-3-aldehyde is obtained in small quantity from the corresponding acetal (*loc. cit.*) by the action of strong hydrochloric acid with subsequent addition of potassium carbonate to the cold diluted solution. It is a colourless oil which boils at 40° under 0.2 mm. pressure; it has a burning taste, fumes with hydrochloric acid, and reduces Fehling's solution. In contact with air, it becomes resinous and insoluble in water. The *platinichloride* crystallises in octahedra.

β -Ethylaminopropaldehyde diethylacetal, $\text{NHEt} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2$, is a by-product in the preparation of the tertiary base (*loc. cit.*). It is a colourless, mobile oil with a basic odour and strongly alkaline reaction. It boils at 82.5–83.5° under 13 mm. pressure. When decomposed by strong hydrochloric acid, it yields the hydrochloride of the aminoaldehyde, $\text{C}_5\text{H}_{11}\text{ON} \cdot \text{HCl}$, which melts at 265–265.5° (*corr.*) and reduces solutions of silver salts.

β -Ethylaminopropaldehyde, $(\text{NHEt} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHO})_3$, is obtained from the hydrochloride by the action of potassium carbonate as a slightly yellow oil, which reduces solutions of silver salts but not Fehling's solution, answers to Schiff's test, and forms with hydrochloric acid a hydrochloride identical with that from which it is prepared. The free aldehyde is remarkably stable, retaining its properties unchanged after being heated in a vacuum to 180°.

C. S.

Reciprocal Stereochemical Influences. HANS MEYER (*Monatsh.*, 1905, 26, 1303–1310).—Two similar or dissimilar groups which influence each other so that they act as if only one group were present, the author terms “conjugated groups.” Typical examples of substances containing “conjugated groups” are the 2- and 4-aminopyridines and the 2- and 4-aminoquinolines, in which the two basic groups influence each other so that salts are formed with only 1 mol. of hydrochloric acid. On treatment with nitrous acid, these bases behave as stable, aliphatic amines.

In 4-aminonicotinic acid, the carboxyl group, and in 4-aminolutidinic acid one of the two carboxyl groups, is partially neutralised by the “conjugated groups”; these acids are therefore *pseudo*-betaines (*Abstr.*, 1904, 25, 490).

On the other hand, in the 3-aminopyridines, 7-aminoquinoline, and 5- and 8-aminoisoquinoline, the tertiary nitrogen and the amino-group have no stereochemical influence on each other, and these bases form

salts with 2 mols. of hydrochloric acid, and when diazotised, behave as aromatic amines.

Similarly, whilst the 3-hydroxypyridines react normally, the 2- and 4-hydroxypyridines (2- and 4-pyridones) and the 2- and 4-hydroxyquinolines do not give the typical reactions. Thus the 2- and 4-pyridones do not yield nitroso-derivatives, cannot be acetylated, do not react normally with phenylcarbimide (Goldschmidt and Meissler, Abstr., 1890, i, 499), and have only feeble salt-forming properties. Claus has shown that on bromination of carbostyryl the "conjugated group" exerts no directive influence (Abstr., 1896, i, 449). G. Y.

Action of Diazomethane on Pyridones and Hydroxypyridinecarboxylic Acids. HANS MEYER (*Monatsh.*, 1905, 26, 1311—1329. Compare preceding abstract).—Whilst 2-pyridone is converted into 2-methoxypyridine only slowly and partially by the action of diazomethane, this reagent interacts energetically with 3-hydroxypyridine, which must be a true hydroxy-compound forming 3-methoxypyridine; this yields a *mercurichloride*, which crystallises in slender, colourless needles and melts at 110°, and a *platinichloride*, which is obtained in yellowish-red crystals and melts at 182°.

The action of diazomethane on 4-pyridone leads to the formation of a mixture of 4-methoxypyridine and 1-methyl-4-pyridone. 4-Methoxypyridine *mercurichloride* crystallises in colourless needles and melts at 191°. Carbostyryl interacts with diazomethane to form 2-methoxyquinoline and not the *N*-methyl derivative.

The action of methyl iodide on 6-hydroxynicotinic acid in aqueous alkaline solution leads to the formation of 6-keto-1-methyl-1:2-dihydropyridine-3-carboxylic acid, which melts at 238—239° (compare von Pechmann and Welsh, Trans., 1885, 47, 150; Abstr., 1885, 174). This differs from all 1-methylpyridinecarboxylic acids investigated previously, as owing to the negative influence of the keto-group on the methylimino-group it does not form the betaine, and can be titrated with *N*/10 potassium hydroxide. When treated with diazomethane, it yields the *methyl* ester, which crystallises in long, glistening needles and melts at 139°.

The action of diazomethane on 6-hydroxynicotinic acid leads to the formation of a mixture of derivatives consisting of 88.5 per cent. of methyl 6-keto-1-methyl-1:2-dihydropyridine-3-carboxylate and 11.5 per cent. of *methyl* 6-methoxynicotinate, $\text{OMe} \cdot \text{C}_5\text{NH}_3 \cdot \text{CO}_2\text{Me}$, which crystallises in soft needles and melts at 122°, whereas diazomethane and methyl 6-hydroxynicotinate interact to form methyl 6-keto-1-methyl-1:2-dihydropyridine-3-carboxylate only.

Methyl 2-hydroxycinchonate is formed from the acid by the action of thionyl chloride or sulphuric acid and methyl alcohol, or together with methyl 2-methoxycinchonate by the action of diazomethane. It crystallises in glistening, colourless needles, melts at 242°, sublimes at 240—250°, and distils apparently without change. *Methyl 2-methoxycinchonate* crystallises in needles, melts at 120°, and has an odour of orange blossoms. When boiled with 2 per cent. aqueous sodium hydroxide, *propionylisatin*, which is formed by boiling isatin with propionic anhydride and melts at 141°, yields 2-hydroxy-3-methyl-

cinchonic acid, $\text{OH} \cdot \text{C}_9\text{NH}_4\text{Me} \cdot \text{CO}_2\text{H}$; this separates from water in colourless crystals, melts at $315\text{--}317^\circ$, and when treated with thionyl chloride and methyl alcohol or with diazomethane yields *methyl 2-hydroxy-3-methylcinchonate*, which crystallises in long, slender needles and melts at $174\text{--}175^\circ$. Prolonged treatment with diazomethane had no further action on the methyl ester.

Chelidamic acid interacts energetically with diazomethane, forming the *dimethyl ester*, $\text{OH} \cdot \text{C}_5\text{NH}_2(\text{CO}_2\text{Me})_2$, which crystallises in long needles, melts at 125° , and is only sparingly soluble in ether.

The author discusses the constitution of comenamic acid (compare Lapworth and Collie, *Trans.*, 1897, **71**, 843; Peratoner, *Abstr.*, 1902, i, 493), and concludes that it is 4:5-dihydroxypyridine-2-carboxylic acid. It does not interact with thionyl chloride (compare *Abstr.*, 1902, i, 31), but when treated with diazomethane yields *methyl 4-hydroxy-5-methoxypyridine-2-carboxylate*, melting at 118° . G. Y.

Formation from Furfuraldehyde of Colouring Matters derived from Pyridine. WILHELM KÖNIG (*J. pr. Chem.*, 1905, [ii], **72**, 555—562. Compare *Abstr.*, 1904, i, 449, 817; Zincke, Heuser, and Möller, *Abstr.*, 1904, i, 921; Zincke and Mühlhausen, this vol., i, 33).—The *hydrobromide* of α -hydroxyglutaconaldehydedianilide, $\text{NHPh} \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{C}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{NHPh}$, HBr , is formed by heating aniline with furfuraldehyde in alcoholic solution on the water-bath, and, after cooling, adding hydrobromic acid of sp. gr. 1.48, diluted with alcohol. It crystallises from acetic acid in prisms which have a deep blue lustre, melts at $164\text{--}165^\circ$, and dyes silk and tannin mordanted cotton-wool deep red or unmordanted cotton-wool rose-red. When heated with nitrobenzene at 150° , it decomposes into aniline and 3-hydroxy-1-phenylpyridinium bromide, which crystallises in white needles containing H_2O and melts at 129° (compare Zincke and Mühlhausen, *loc. cit.*). The picrate, $\text{C}_{17}\text{H}_{12}\text{O}_8\text{N}_4$, crystallises in slender, yellow needles and melts at 219° .

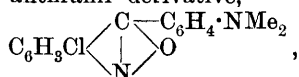
The *hydrobromide* of α -hydroxyglutaconaldehydedi-*p*-phenetide, $\text{C}_{21}\text{H}_{26}\text{O}_4\text{N}_2$, HBr , formed from *p*-phenetidine and furfuraldehyde by the same method as the dianilide, crystallises in glistening, blue prisms, melts at $157\text{--}158^\circ$, and dyes silk and unmordanted cotton-wool the rhodamine colour, but not fast. The free *base* is obtained as a yellow, oily mass. When heated with nitrobenzene, it yields 3-hydroxy-1-*p*-ethoxyphenylpyridinium bromide, $\text{C}_{13}\text{H}_{14}\text{O}_2\text{NBr}$, H_2O , which crystallises in colourless, iridescent leaflets and melts at $167\text{--}168^\circ$. The *picrate* forms yellow needles and melts at 207° . G. Y.

Dyes derived from Furfuraldehyde. WALTER DIECKMANN and LUDWIG BECK [and, in part, BRUNO SZELINSKI] (*Ber.*, 1905, **38**, 4122—4125. Compare Zincke and Mühlhausen, this vol., i, 33; König, preceding abstract).—Hydroxyglutaconaldehydedianilide hydrobromide, $\text{NHPh} \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{C}(\text{OH}) \cdot \text{CH} : \text{NPh}$, HBr , H_2O , prepared either by the action of aniline and aniline hydrobromide on furfuraldehyde or by the action of aniline and cyanogen bromide on 3-hydroxypyridine, melts and decomposes at 166° and is converted by heating with alcohol and hydrochloric acid into 3-hydroxy-1-phenylpyridinium chloride, $\text{OH} \cdot \text{C}_5\text{NH}_4\text{PhBr}$, which melts and decomposes at

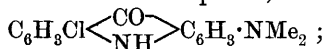
210° and yields a *picrate* melting and decomposing at 218—221° and a *platinichloride* melting and decomposing at 199°; the identity of the two preparations is thus fully demonstrated.

Similar evidence was obtained in the case of the *p*-chloroaniline derivatives. *Hydroxyglutaconaldehydedi-p-chloroanilide hydrochloride*, $C_6H_4Cl \cdot NH \cdot CH : CH : CH : C(OH) \cdot CH : N \cdot C_6H_4Cl, HCl$, resembles the dianilide hydrochloride and melts and decomposes at 167°. *3-Hydroxy-1-p-chlorophenylpyridinium chloride*, $OH \cdot C_5NH_4Cl \cdot C_6H_4Cl$, crystallises from water in long, colourless needles and melts and decomposes at 221°. The *platinichloride* crystallises from hot water in orange-yellow needles and melts and decomposes at 217°. T. M. L.

Action of *o*-Nitrobenzaldehyde on Dimethylaniline in Presence of Hydrochloric Acid. THEODOR ZINCKE and WILHELM PRENTZELL (*Ber.*, 1905, 38, 4116—4122).—*o*-Nitrobenzaldehyde and dimethylaniline, which yield a triphenylmethane compound when acted on by zinc chloride, give, when acted on by concentrated hydrochloric acid at 110—115°, a compound, $C_{15}H_{13}ON_2Cl$, which is formulated as an anthranil derivative,

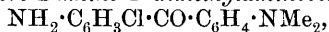


but might possibly be an acridone compound,



it crystallises from hot alcohol in yellow needles, from acetone in stout, reddish-yellow needles, and melts at 162—163°; its dilute alcoholic and ethereal solutions show a very strong fluorescence, similar to that of fluorescein; concentrated solutions are yellow; it is stable towards alkali hydroxides and does not lose chlorine, but has slight basic properties. The *hydrochloride* forms colourless flakes, the *nitrate* and *sulphate* colourless needles; the *platinichloride*, $(C_{15}H_{13}ON_2Cl)_2 \cdot H_2PtCl_6$, crystallises in minute, yellow scales, is insoluble in water, and decomposes above 200°; the *methiodide*, $C_{15}H_{13}ON_2Cl, MeI$, crystallises from hot alcohol in glistening scales, melts at 184° liberating methyl iodide, and fluoresces in alcoholic solution.

Reduction by means of zinc and acetic acid gives a compound formulated as 5-chloro-2-amino-4'-dimethylaminobenzophenone,



which crystallises in minute, yellow needles and melts at 185°. The *hydrochloride* crystallises from dilute hydrochloric acid in colourless, glistening tablets, but is decomposed by water or alcohol. The *acetyl* derivative crystallises from dilute alcohol in yellow, glistening needles and melts at 132°. The ketone is reduced by hydrogen iodide and phosphorus at 190—200° to 2:4'-diaminodiphenylmethane (Stadel, *Abstr.*, 1895, i, 233), which crystallises from ether in transparent tablets, melts at 88—89°, and is readily converted into diphenylmethane. The *hydrochloride* crystallises in small, colourless needles. The acetyl derivative separates from alcohol in white, tabular crystals melting at 208°, or in small, glistening needles melting at 218°; only the latter modification is described by Stadel. T. M. L.

Phenylhydrazine as a Reducing Agent in Organic Chemistry. GIUSEPPE PLANCHER (*Gazzetta*, 1905, 35, ii, 460—463).—Polemical. A reply to Oddo and Puxeddu (*Abstr.*, 1905, i, 842).
T. H. P.

Phenylethylidenehydrazine. GEORG LOCKEMANN and OTTO LIESCHE (*Annalen*, 1905, 342, 14—50).—Phenylethylidenehydrazine, that is, acetaldehydephenylhydrazone, was used in the preparation of acetaldehyde as a means of recognising acetaldehyde (*Abstr.*, 1905, i, 570). It has been shown by Fischer (*Abstr.*, 1896, i, 361) to exist in two or three mutually convertible isomeric forms. A list is given of the phenylhydrazones of aldehydes or ketones or ketonic acids, of osazones, of diketones, and other similar hydrazones which exhibit isomerism. This isomerism has been variously regarded as a structural or steric isomerism, but the explanation given by Hantzsch, and based on the latter type of isomerism, is regarded as the most adequate.

The conditions under which the two forms of the acetaldehydephenylhydrazone are stable have been investigated. Fischer (*loc. cit.*) obtained a β -form (m. p. 63—65°), which was transformed by alcoholic sodium hydroxide into the α -form, melting at 98—101°; the latter then passed slowly into a third variety melting at 80°. It is now found that this substance exists in two modifications; the stable α -variety melts at 98—101°, whilst the labile β -form melts at 57°. The β -hydrazone gradually changes into the α -form, but the transformation is hastened by the action of bases, such as sodium hydroxide or ammonia, and also by various salts. Crystallisation from alkaline 75 per cent. alcohol is the most effectual method. The change from the α - into the β -form also takes place in certain solvents, but is momentarily effected by treatment with aqueous sulphurous acid. The depression of the freezing point of the α -modification does not appear to be due to a conversion into a third form, but to decomposition, oxidation, &c. Fischer's isomeride (m. p. 63—65°) is probably an amorphous mixture of the α - and β -hydrazones.

Acetaldehydephenylhydrazone is prepared by adding molten phenylhydrazine to an ice-cold solution of acetaldehyde in light petroleum. The product, which is white, can only be kept in an atmosphere free from alkaline or acid vapours; it melts usually at 51—57°, although higher melting points (98°) have been observed. On crystallisation from 75 per cent. alcohol containing a trace of sodium hydroxide, prismatic crystals of the α -modification are obtained.

The β -modification is obtained by adding aqueous sulphurous acid either to a 75 per cent. alcoholic solution of the α -hydrazone or by moistening the crystals. The use of a stronger acid, hydrochloric or nitric, brings about the transformation, but at the same time causes some decomposition. Carbon dioxide attacks the α -modification slowly, but does not convert it into the β -form. Even in a completely neutral medium, such as air, the β -modification becomes coloured, and the melting point rises.

Indifferent solvents cause the transformation of either form into the other, but in no case can a complete transformation be effected by simple

recrystallisation. The melting point of the β -form may be somewhat raised by recrystallisation or that of the α -form somewhat lowered.

Both isomerides show the same behaviour towards benzoyl chloride. Dibenzoylphenylhydrazine (m. p. 177—178°) is formed when an aqueous suspension of the hydrazone is treated with benzoyl chloride and sodium hydroxide; at the same time *tribenzoylphenylhydrazine*, $C_{27}H_{20}O_3N_2$, is formed; it can be prepared by repeated treatment of phenylhydrazine with benzoyl chloride in ethereal solution in the presence of sodium hydroxide, and crystallises in rhombic plates melting at 200—201°. Both the α - and β -hydrazones yield the same β -benzoyl- β -phenyl- α -ethylidenehydrazine, $CHMe:N \cdot NPhBz$, when the benzylation is carried out in pyridine solution; it crystallises in rectangular plates or cubes melting at 89—90°, and is reduced by zinc dust and acetic acid to benzanilide. It does not condense under the action of phosphoric oxide or zinc chloride to a diphenylpyrazole.

It is thought that the isomerism of acetaldehydephenylhydrazone is not explicable from a stereochemical standpoint, but rather is better accounted for as a case of tautomerism. K. J. P. O.

Diphenylhydrazine, Hydrazobenzene, and Benzylaniline, and Miscibility of the last two with Azobenzene, Stilbene, and Dibenzyl in the Solid State. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 466—474).—The following crystallographic constants were determined: *as*-diphenylhydrazine, triclinic [$a:b:c = 0.7698:1:0.5986$; $\alpha = 89^\circ 24'$, $\beta = 137^\circ 28.5'$, $\gamma = 90^\circ 4.5'$]; hydrazobenzene, rhombic [$a:b:c = 0.9787:1:1.2497$]; benzylaniline, monoclinic [$a:b:c = 2.1076:1:1.6422$; $\beta = 76^\circ 36.5'$].

Bruni and Gorni (*Abstr.*, 1899, ii, 407, 732) and Garelli and Calzolari (*Abstr.*, 1899, ii, 732; 1900, ii, 65) have concluded from freezing-point observations that mixed crystals are formed between dibenzyl, stilbene, tolane, and azobenzene, the groups $-CH_2 \cdot CH_2-$, $-CH:CH-$, $-C:C$, and $-N:N-$ being capable of mutual replacement in an isomorphous series, a conclusion which has been confirmed by the crystallographic measurements of Boeris (*Atti Soc. Ital. Sci. Milano*, 1900, 39, 111—123). It has therefore been suggested that if two aromatic substances can form mixed crystals, their hydro-products can do the same. This conclusion is contradicted by the marked contrast between hydrazobenzene (rhombic) and azobenzene (monoclinic), which are not isomorphous, do not form mixed crystals, and give the normal V-shaped melting-point curve; the group $-NH:NH-$ must therefore be excluded from the above series. Benzylaniline, containing the mixed group $-CH_2 \cdot NH-$, might be expected to fall in with the rest of the series; actually, although not isomorphous with azobenzene, a rearrangement of the indices gives very similar values for $a:b$ and for β , but different values for $c:b$; the relationship is therefore morphotropic but not isomorphous. T. M. L.

Action of Nessler's Solution on Antipyrine, Pyramidone, Antifebrin, and Exalgin. PAUL N. RAIKOW and CHR. KÜLÜMOW (*Chem. Centr.*, 1905, ii, 1595; from *Oesterr. Chem. Zeit.*, [ii], 8, 445—448. Compare Schuyten, *Abstr.*, 1898, i, 452; Ville and Astre, *Abstr.*, 1900, i, 362, 411).—The author has succeeded in preparing

mercuric iodide compounds of antipyrine, pyramidone, antifebrin, and exalgin by using alkaline solutions of mercuric iodide.

"Antipyrine oil" forms a bright yellow, somewhat viscous liquid and has a sp. gr. 1.3518 at 19°; it is readily soluble in alcohol or acetone, less so in water, and insoluble in ether, carbon disulphide, chloroform, or alkalis. The aqueous solution is alkaline. The compound is decomposed when treated with water which has not been distilled, or by boiling the solution in distilled water, a white precipitate being formed in each case; hydrochloric and sulphuric acids also give precipitates. Antipyrine oil is not volatile and is decomposed when strongly heated. With concentrated sulphuric acid, it gives a red coloration, and on warming the mixture small, red crystals are formed and iodine liberated. By the action of hydrogen sulphide, silver nitrate, and an excess of silver nitrate on a solution of the oil in acetone, mercuric sulphide, mercuric iodide, and silver iodide are formed respectively; when heated with acetic acid, a compound, $\text{Hg}\left[\text{N}(\text{I})\left\langle\begin{array}{c} \text{NPh}\cdot\text{CO} \\ \text{CMe}\cdot\text{CH} \end{array}\right\rangle\right]_2$, is formed, which crystallises in pale yellow, prismatic crystals, melts at 133°, and is decomposed by repeated crystallisation from glacial acetic acid. It is soluble in acetone, chloroform, or glacial acetic acid, but insoluble in cold water, ether, or carbon disulphide. When heated with water, it becomes deep yellow, but regains its original colour on cooling; the warm aqueous solution is neutral.

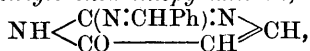
The compound $\text{HgI}\cdot\text{N}(\text{I})\cdot\text{CMe}\left\langle\begin{array}{c} \text{NPh}\cdot\text{CO} \\ \text{C}\cdot\text{NHMe}_2\text{I} \end{array}\right\rangle$ (?), formed by the action of Nessler's reagent on dimethylaminoantipyrine (pyramidone), crystallises from acetic acid in sulphur-yellow needles and melts at 170—172°; it is readily soluble in acetone or hot acetic acid, sparingly so in water, and insoluble in ether, chloroform, or benzene. The aqueous solution is neutral to litmus. Acetanilide (antifebrin) is only partially attacked by Nessler's reagent, a yellow mercuric iodide compound being formed which is insoluble in ether, chloroform, or alcohol, and is decomposed by water with liberation of mercuric iodide.

The yellow oil, "exalgin oil," $\text{HgI}\cdot\text{NPhMeI}\cdot\text{COMe}$ or $\text{Hg}_2(\text{NPhIme}\cdot\text{COMe})_2\cdot 2\text{HI}$, obtained by the action of Nessler's reagent on methylacetanilide (exalgin), gradually becomes darker; it is miscible with a small quantity of water. By the action of a large quantity of water on the oil, yellow mercuric iodide is formed, and the liquid becomes opaque; after a time, however, red mercuric iodide separates out and the liquid regains its transparency and becomes almost colourless. When water or ether is added to a solution of the oil in acetic acid, red mercuric iodide is formed. The oil is insoluble in carbon disulphide and is partially decomposed by light petroleum, regenerating its components; by the action of concentrated sulphuric or nitric acid, exalgin and iodine are formed. E. W. W.

Pyrimidines; 2:5-Diamino-6-oxypyrimidine. XII. TREAT B. JOHNSON and CARL O. JOHNS (Amer. Chem. J., 1905, 34, 554—568).—5-Nitro-2-amino-6-oxypyrimidine, $\text{NH}\left\langle\begin{array}{c} \text{C}(\text{NH}_2):\text{N} \\ \text{CO}\cdot\text{C}(\text{NO}_2) \end{array}\right\rangle\text{CH}$, obtained by

the nitration of 2-amino-6-oxypyrimidine (*isocytosine*) (Wheeler and Johnson, Abstr., 1903, i, 526), crystallises in groups of yellow, microscopic prisms, becomes brown at about 280°, does not decompose below 300°, and is insoluble in the usual organic solvents; when heated for four hours at 190—200° with dilute sulphuric acid, it is converted into nitrouracil. When 5-nitro-2-amino-6-oxypyrimidine is reduced with aluminium amalgam in presence of ammonia, 2:5-diamino-6-oxypyrimidine, $\text{NH} \begin{smallmatrix} \text{C}(\text{NH}_2)=\text{N} \\ \text{CO} \cdot \text{C}(\text{NH}_2) \end{smallmatrix} \text{CH}_2\text{H}_2\text{O}$, is produced, which crystallises in large, radiating prisms, is very soluble in water, and is probably identical with the diamino-oxypyrimidine obtained by Kutscher (Abstr., 1903, i, 668) from the nucleic acid of yeast. The anhydrous base decomposes at about 245° and has no definite melting point. The *picrate*, *hydrochloride*, *nitrate*, and *sulphate* are described. When 2:5-diamino-6-oxypyrimidine is heated with 20 per cent. sulphuric acid for three hours at 130—140° in a sealed tube, it is partially converted into 2-amino-5:6-dioxypyrimidine, which crystallises from water in groups of microscopic prisms and does not decompose below 300°; its *picrate* is described.

2:5-Diamino-6-oxypyrimidine may also be prepared by heating 5-bromo-2-amino-6-oxypyrimidine with concentrated solution of ammonia or by the action of alcoholic ammonia on 5-amino-6-oxypyrimidine. When an aqueous solution of guanidine is heated with ethyl sodioformylhippurate, 2-amino-6-oxypyrimidine, $\text{NH} \begin{smallmatrix} \text{C}(\text{NH}_2)=\text{N} \\ \text{CO} \cdot \text{C}(\text{NH}_2) \end{smallmatrix} \text{CH}_2\text{H}_2\text{O}$, is produced, which crystallises from hot water in microscopic needles and decomposes at about 275°. By the action of benzaldehyde on 2-amino-6-oxypyrimidine, 6-oxypyrimidine-2-benzylideneaminopyrimidine,



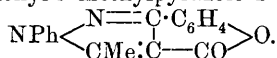
is obtained, which forms yellow crystals, decomposes at 238—242°, and is very stable towards nitric acid. When a solution of 2-amino-6-oxypyrimidine in acetic acid is treated with sodium nitrite, a *substance* is formed which crystallises in microscopic prisms, is very soluble in water, turns brown at about 280°, does not melt below 300°, and is probably an acetate of 2-amino-6-oxypyrimidine. E. G.

New General Method of Synthesising Pyrazole Derivatives.

GAETANO MINUNNI [in part with G. VASSALLO, RICCARDO CIUSA, and GUIDO LAZZARINI] (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 414—420). —On heating a mixture of equal quantities of benzaldehydephenylhydrazone and ethyl acetoacetate at 195—205°, a *substance*, $\text{C}_{21}\text{H}_{16}\text{O}_2\text{N}_2$, is obtained which crystallises from alcohol in white, nacreous laminae melting at 140—140.5°, and is soluble in ether, light petroleum, or amyl alcohol, and very readily so in ethyl acetate, benzene, or chloroform. It dissolves in cold concentrated sulphuric acid, imparting to it an intense red coloration, and when boiled with concentrated potassium hydroxide solution is converted into a *substance* which separates from alcohol in white crystals melting at 112—113°. With bromine in chloroform solution, it gives a compound which crystallises

from alcohol in long, white needles melting at 160° , and contains 20.5 per cent. of bromine. Later attempts to prepare the substance $C_{21}H_{16}O_2N_2$ from other samples of ethyl acetoacetate have proved fruitless, and its constitution has not been determined.

The condensation of benzaldehydephenylhydrazone and ethyl acetoacetate in presence of zinc chloride yields ethyl 1:3-diphenyl-5-methylpyrazole-4-carboxylate (Knorr and Blank, Abstr., 1885, 810). Similarly, the condensation of salicylaldehydephenylhydrazone with ethyl acetoacetate in presence of zinc chloride leads first to the formation of ethyl 1-phenyl-3-hydroxyphenyl-5-methylpyrazole-4-carboxylate, which loses one mol. of ethyl alcohol, giving the lactone of 1-phenyl-3-hydroxyphenyl-5-methylpyrazole-4-carboxylic acid,



By alcoholic potassium hydroxide solution, this lactone is transformed into the acid, which is readily reconverted into the lactone by heating or by the action of acid chlorides. The phenylhydrazone of *m*-(or *p*)-nitrobenzaldehyde, when condensed with ethyl acetoacetate in presence of zinc chloride, yields ethyl 1-phenyl-3-*m*-(or *p*)-nitrophenyl-5-methylpyrazole-4-carboxylate.

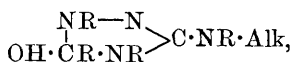
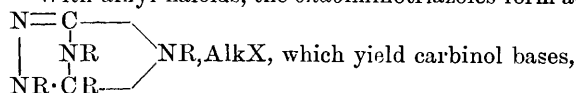
T. H. P.

*endo*Iminotriazoles. II. MAX BUSCH and GUSTAV MEHRTENS (*Ber.*, 1905, 38, 4049—4068. Compare Abstr., 1905, i, 307).—The action of aldehydes on triarylaminoguanidines leads to the formation

of aminodihydrotriazoles, $\begin{array}{c} NR \\ | \\ CHR \cdot NR \end{array} \begin{array}{c} \diagup N \\ \diagdown N \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} C \cdot NHR$, which are decomposed

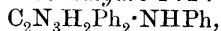
by mineral acids and on oxidation yield *endo*iminotriazoles, which are formed also by the action of acetic and benzoic acids on triarylaminoguanidines in presence of phosphorus pentachloride, but not of the acids alone; they form sparingly soluble nitrates.

With alkyl haloids, the *endo*iminotriazoles form additive compounds,



and when heated with potassium hydroxide are decomposed with rupture of the cyclic nucleus.

3-Anilino-1:4-diphenyl-4:5-dihydro-1:2:4-triazole,

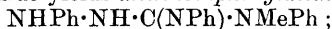


formed by the action of formaldehyde on triphenylaminoguanidine in boiling alcoholic solution, crystallises in stout, white, glistening needles, melts at 128° , is easily soluble in chloroform, ether, benzene, or hot alcohol, and yields formaldehyde when heated with dilute sulphuric acid. When oxidised with alcoholic ferric chloride or sodium nitrite in alcoholic-acetic acid solution, it yields 1:4-diphenyl-3:5-*endo*anilodihydrotriazole, which the author terms "nitron." This forms a *picrate*, $C_{26}H_{19}O_7N_7$, which crystallises in sheaves of small needles and melts at 257 — 258° , and a *dichloride*, $C_{20}H_{16}N_4 \cdot 2HCl$, which crystallises in glistening, white leaflets and commences to

decompose at 160°. The *methiodide*, $\begin{array}{c} \text{N}=\text{C} \\ | \quad \diagup \\ \text{NPh} \quad \text{NPh} \\ | \quad \diagdown \\ \text{NPh} \cdot \text{CH} \end{array} \text{NPh,MeI}$, formed

by heating nitron with an excess of methyl iodide in a reflux apparatus fitted with a mercury valve, crystallises from alcohol in yellow plates, or from water in glistening needles, melts at 211—213°, and has the conductivity $\mu_{27.2} = 85$ at 25°.

The aqueous solution of the methiodide becomes neutral immediately on addition of sodium hydroxide, but in dilute alcoholic solution the isomeric change from the strongly alkaline ammonium base first formed, into the carbinol base takes place more slowly, and is represented by the gradually diminishing alkalinity of the solution. The action of sodium hydroxide leads, further, to the hydrolysis of the carbinol base and formation of a red *azo*-compound, which on reduction with hydrogen sulphide yields *anilinodiphenylmethylguanidine*,

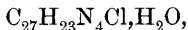


this crystallises in sheaves of needles, melts at 96—97°, is readily soluble in benzene or ether, and is oxidised in alcoholic solution by the air, becoming red.

The *carbinol* base (*5-hydroxy-3-methylanilino-1:4-diphenyl-4:5-dihydro-1:2:4-triazole*), $\begin{array}{c} \text{NPh} \text{---} \text{N} \\ | \quad \diagup \\ \text{CH}(\text{OH}) \cdot \text{NPh} \end{array} \text{C} \cdot \text{NMePh}$, is prepared by

treating the methiodide with aqueous ammonia; it forms a yellow powder, melts at 65°, is readily soluble in alcohol, ether, or benzene, and on treatment with nitric acid in dilute acetic acid solution forms the *methonitrate*, $\text{C}_{21}\text{H}_{19}\text{N}_4 \cdot \text{NO}_3$, which crystallises in glistening, clear, flat needles and melts at 160°. The *methopicrate*, $\text{C}_{21}\text{H}_{19}\text{N}_4 \cdot \text{C}_6\text{H}_2\text{O}_7\text{N}_3$, formed by the action of picric acid on the carbinol base in dilute acetic acid solution or on the methiodide in alcoholic solution, crystallises in long, glistening needles and melts at 193°.

The *additive* compound of nitron and benzyl chloride,



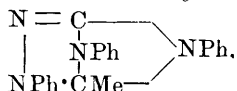
crystallises in clear, thick, tetragonal plates, sinters slightly at 180°, melts at 210°, is readily soluble in alcohol or warm water, forming neutral solutions, has the conductivity $\mu_{10} = 60$ at 25°, and exhibits the same behaviour as the methiodide on treatment with alkali hydroxides. The *hydrochloride*, $\text{C}_{27}\text{H}_{23}\text{N}_4\text{Cl} \cdot \text{HCl}$, crystallises in colourless needles, softens at 150°, and melts and decomposes at 160°; the *nitrate*, $\text{C}_{27}\text{H}_{23}\text{O}_3\text{N}_5$, crystallises in white needles, sinters at 209°, and decomposes suddenly at a few degrees higher. The *carbinol* base (*5-hydroxy-3-benzylanilino-1:4-diphenyl-4:5-dihydro-1:2:4-triazole*), $\text{C}_{27}\text{H}_{24}\text{ON}_4$, formed by the action of aqueous ammonia on the chloride, crystallises in glistening, transparent, short, tetragonal prisms, melts at 153°, is only sparingly soluble in alcohol, ether, or benzene, and on treatment with alcoholic hydrogen chloride is converted into a mixture of the benzyl chloride additive compound and its hydrochloride.

Anilinodiphenylbenzylguanidine, $\text{NPh} \cdot \text{NH} \cdot \text{C}(\text{NPh}) \cdot \text{NPh} \cdot \text{CH}_2\text{Ph}$, formed by the action of sodium hydroxide on the benzyl chloride additive compound, crystallises in nodular aggregates of needles, melts

at 153° , and is oxidised on exposure to the air, with formation of the red *azo*-compound.

3-*Anilino*-1 : 4-*diphenyl*-5-*methyl*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*,
 $C_2N_3HMePh_2 \cdot NHPh$,

formed from triphenylaminoguanidine and acetaldehyde, crystallises from alcohol in glistening, white leaflets, melts at 131° , is readily soluble in chloroform, ether, or benzene, and on oxidation yields 1 : 4-*diphenyl*-5-*methyl*-3 : 5-*endoanilo*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*,



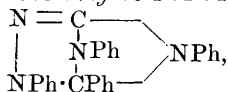
which is formed also by boiling triphenylaminoguanidine with acetyl chloride in a reflux apparatus. It crystallises in moss-like aggregates of yellow needles, melts at $245-246^{\circ}$, is moderately soluble in methyl alcohol, acetone, or chloroform, forms easily soluble salts, and is decomposed by alcoholic alkali hydroxides, forming acetic acid and triphenylaminoguanidine. The *platinichloride*, $(C_{21}H_{18}N_4)_2, H_2PtCl_6$, forms microcrystalline leaflets and melts at $180-181^{\circ}$.

1 : 4-*Diphenyl*-5-*ethyl*-3 : 5-*endoanilo*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*,
 $C_{22}H_{20}N_4$,

formed by heating triphenylaminoguanidine with propionic chloride at 120° and finally at 140° , crystallises from dilute alcohol in long, brown, rectangular plates, melts at $229-230^{\circ}$, is moderately soluble in boiling benzene or chloroform, and readily so in dilute sulphuric or acetic acids.

3-*Anilino*-1 : 4 : 5-*triphenyl*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*,
 $C_2N_3HPh_3 \cdot NHPh$,

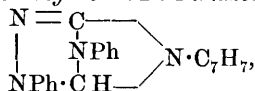
formed from triphenylaminoguanidine and benzaldehyde, crystallises from alcohol in colourless needles, melts at 165° , is readily soluble in chloroform, ether, or benzene, yields an odour of benzaldehyde, and when oxidised with sodium nitrite in acetic acid solution yields 1 : 4 : 5-*triphenyl*-3 : 5-*endoanilo*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*,



which is formed also by heating triphenylaminoguanidine with benzoic chloride at 130° or by boiling the guanidine with benzoic acid and phosphorus pentachloride. It crystallises from alcohol in glistening, dark yellow, flat needles, melts at $231-232^{\circ}$, and forms an *additive* compound with benzoic chloride, $C_{23}H_{25}ON_4Cl$, which crystallises from ether in colourless needles, melts and decomposes with formation of benzoic chloride at about 262° , and when dissolved in alcohol yields triphenylendoanilodihydrotriazole hydrochloride and ethyl benzoate, or benzamide when treated with alcoholic ammonia. The *nitrate*, $C_{26}H_{20}N_4, HNO_3$, crystallises from boiling water in colourless needles and melts above 270° ; the *hydrochloride* forms sheaves of colourless, flat needles and melts at 270° . The *methiodide*, $C_{26}H_{20}N_4, MeI$, crystallises from its ethereal-alcoholic solution in colourless needles, melts at 231° , and is readily soluble in alcohol or chloroform.

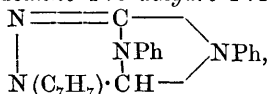
5-Hydroxy-3-methylanilino-1:4:5-triphenyl-4:5-dihydro-1:2:4-triazole, $\text{OH} \cdot \text{C}_6\text{H}_3\text{N}_3 \cdot \text{Ph}_3 \cdot \text{NMePh}$, formed by the action of potassium hydroxide on the methide in ice-cooled absolute alcoholic solution, crystallises from a mixture of light petroleum and chloroform in yellow, hexagonal leaflets, melts at 158° , is readily soluble in chloroform, and when treated with dilute hydrochloric acid yields the *methochloride*, $\text{C}_{27}\text{H}_{23}\text{N}_4\text{Cl}$, which crystallises in spherical aggregates of white needles and melts above 265° .

Anilinophenyl-p-tolylguanidine, $\text{NHPh} \cdot \text{NH} \cdot \text{C}(\text{NPh}) \cdot \text{NH} \cdot \text{C}_7\text{H}_7$, formed from phenylhydrazine and carbodiphenylimide, crystallises in spherical aggregates of needles, melts at $184\text{--}185^\circ$, and condenses with formaldehyde to form *3-anilino-1-phenyl-4-p-tolyl-4:5-dihydro-1:2:4-triazole*, $\text{C}_{21}\text{H}_{20}\text{N}_4$, which crystallises in colourless needles and melts at 148° . On oxidation with sodium nitrite, it yields a *1-phenyl-4-p-tolyl-3:5-endoanilo-4:5-dihydro-1:2:4-triazole*,



which crystallises from a mixture of chloroform and light petroleum in dark yellow needles and melts at 210° .

3-Anilino-4-phenyl-1-p-tolyl-4:5-dihydro-1:2:4-triazole, $\text{C}_{21}\text{H}_{20}\text{N}_4$, formed from formaldehyde and *p*-toluidinodiphenylguanidine, crystallises from alcohol in glistening leaflets, melts at 123° , is easily soluble in benzene or chloroform, and on oxidation with nitrous acid yields *4-phenyl-1-p-tolyl-3:5-endoanilo-4:5-dihydro-1:2:4-triazole*,



which crystallises in matted, glistening, light yellow needles and melts at 222° .

3-Toluidino-1-phenyl-4-p-tolyl-4:5-dihydro-1:2:4-triazole, $\text{C}_{22}\text{H}_{22}\text{N}_4$, formed from formaldehyde and anilinditolylguanidine, crystallises in matted, long, white needles, melts at 132° , and on oxidation yields *1-phenyl-4-p-tolyl-3:5-endotoluido-4:5-dihydro-1:2:4-triazole*, $\text{C}_{22}\text{H}_{20}\text{N}_4$, which forms glistening, yellow needles, melts at 170° , and is readily soluble in chloroform.

It has been found that as a test for nitrates nitron is even more delicate than was stated previously (Abstr., 1905, ii, 282).

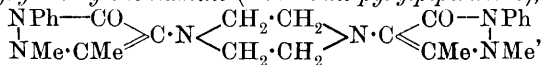
G. Y.

Synthetical Bases from 4-Aminoantipyrine. MAX LUFT (*Ber.*, 1905, 38, 4044—4049. Compare Knorr and Stolz, Abstr., 1897, i, 112).—*Diantipyrylethylenediamine*, $\text{C}_2\text{H}_4(\text{NH} \cdot \text{C} \begin{array}{l} \text{CO-NPh} \\ \text{CMe-NMe} \end{array})_2$, is

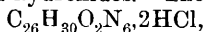
formed when 2 mols. of 4-aminoantipyrine are heated with 1 mol. of ethylene dibromide in alcoholic solution on the water-bath, and 20 per cent. aqueous sodium hydroxide is added until the mixture is alkaline. It separates from a mixture of chloroform and ether as a colourless, flocculent powder, melts at 54° , is extremely hygroscopic, absorbs

carbon dioxide from the atmosphere, and is precipitated unchanged on addition of alkali hydroxides to its acid solutions. The *platinichloride*, $C_{24}H_{28}O_2N_6H_2PtCl_6$, forms orange needles and decomposes at $206-208^\circ$; the *picrate* crystallises in yellow needles and melts at 182° ; the *mercurichloride* is insoluble in water and decomposes at $70-72^\circ$.

Diantipyrilydiethylenediamine (1 : 4-diantipyrilpiperazine),



formed by the action of an excess of ethylene dibromide on antipyrine or on diantipyrilethylenediamine at $120-130^\circ$, crystallises from alcohol in colourless, nacreous, rhombic plates or needles, melts at 262° , is only sparingly soluble or is insoluble in all solvents, and is very stable towards alkali hydroxides. The *hydrochloride*,

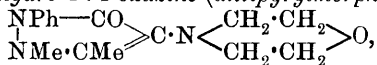


crystallises in colourless needles and melts at 248° ; the *hydrobromide* melts at 237° ; the *platinichloride*, $C_{26}H_{30}O_2N_6H_2PtCl_6$, forms yellow needles, becomes grey at 100° , and decomposes at about 145° ; the *mercurichloride* melts at 231° .

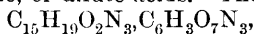
1-Antipyrilpiperidine, $\begin{array}{c} \text{NPh}-\text{CO} \\ | \\ \text{NMe}\cdot\text{CMe} \end{array} \geq \text{C}\cdot\text{N} \begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{array} > \text{CH}_2$, formed

by heating 4-aminoantipyrine with $\alpha\epsilon$ -dibromopentane at 100° , crystallises from ether in colourless needles, has an odour of piperidine, melts at 144° , is soluble in alcohol, ether, benzene, or dilute acids, and is stable towards alkali hydroxides. The *hydrochloride* is deliquescent; the *hydriodide*, $C_{16}H_{21}ON_3HI$, crystallises in glistening, yellow needles and decomposes with evolution of a gas at 215° ; the *picrate* forms glistening, yellow prisms and melts and decomposes at 198° ; the *platinichloride*, $C_{33}H_{42}O_2N_6H_2PtCl_6$, forms plates and melts and decomposes at $208-210^\circ$; the *mercurichloride* crystallises in white, rhombic plates and melts and decomposes at 204° ; the *methiodide* is obtained as a brown oil which solidifies to a yellow mass; it melts at 206° and decomposes when warmed with water.

1-Antipyriltetrahydro-1 : 4-oxazine (*antipyrilmorpholine*),



is obtained by digestion of 4-aminoantipyrine with ethylene oxide or ethylene bromohydrin in aqueous solution in a sealed tube for two days at the laboratory temperature, and then for fourteen hours at 60° , and heating the yellow, oily product with 50 per cent. sulphuric acid at $125-135^\circ$ under pressure. The intermediately formed hydroxyethyl- and dihydroxyethyl-aminoantipyrine could not be isolated. The morpholine derivative crystallises in rosettes of long, colourless needles, has an aromatic odour, melts at 157° , and is soluble in alcohol, ether, benzene, or dilute acids. The *picrate*,

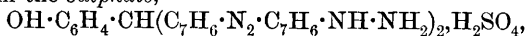


crystallises in yellow plates and melts at 172° ; the white, crystalline *mercurichloride* melts and decomposes at 201° ; the *methiodide*, $C_{15}H_{19}O_2N_3\cdot MeI$, crystallises in colourless needles, melts at 134° , and decomposes when warmed with water.

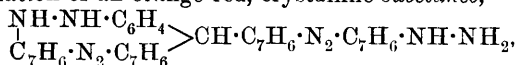
G. Y.

Action of Sulphur Dioxide on *m*-Toluenediazonium Chloride and Benzenediazonium Sulphate. JULIUS TRÖGER, W. HILLE, and P. VASTERLING (*J. pr. Chem.*, 1905, [ii], 72, 511—535. Compare Abstr., 1904, i, 118).—The red sulphonic acid formed by the action of sulphur dioxide on diazotised *m*-toluidine is considered now to have the constitution $C_7H_7 \cdot N_2 \cdot C_7H_6 \cdot NH \cdot NH \cdot SO_3H$. It yields sulphuric acid when hydrolysed with aqueous hydrochloric acid and potassium sulphite with dilute potassium hydroxide, whilst reduction with stannous chloride and hydrochloric acid leads to the formation of sulphuric acid, ammonia, *m*-toluidine, and a tolylenediamine. The potassium salt is oxidised by mercuric oxide in aqueous solution with formation of the *potassium* salt, $C_7H_7 \cdot N_2 \cdot C_7H_6 \cdot N_2 \cdot SO_3K$, which does not give a red coloration on acidification and is reduced to the original sulphonate by ammonium sulphide. The colourless *sulphonic acid*, $C_{14}H_{14}O_3N_4S$, forms stable *silver*, *barium*, and *calcium* salts, whereas the red sulphonic acid reduces warm ammoniacal silver solutions.

The action of nitrous acid on the red sulphonic acid leads to the formation of a *derivative*, $C_7H_7 \cdot N_2 \cdot C_7H_6 \cdot N_3$ (?), which forms short, dark red prisms or small, orange-red crystals and melts at 65°. The sulphonic acid condenses with salicylaldehyde in presence of sulphuric acid to form the *sulphate*,



which is obtained in microscopic needles having a green sheen and dissolves in water to form a violet-blue solution. The *hydrochloride*, $C_{35}H_{36}ON_8 \cdot HCl$, and the *nitrate*, $C_{35}H_{36}ON_8 \cdot HNO_3$, formed by condensation of the sulphonic acid with salicylaldehyde in presence of hydrochloric and nitric acids respectively, have similar properties. The action of ammonia on the salts of the condensation product leads to the formation of an orange-red, crystalline *substance*,



which melts at 130° and forms dark-coloured, crystalline salts with strong acids. The red sulphonic acid forms similar condensation *products* with other fatty and aromatic aldehydes and with ketones.

When a current of sulphur dioxide is passed through a cooled aqueous solution of benzenediazonium sulphate for one day, the *sulphonic acid*, $N_2Ph \cdot C_6H_4 \cdot NH \cdot NH \cdot SO_3H$, is formed as a voluminous, red mass (compare Koenigs, Abstr., 1878, 219). It crystallises in microscopic, dark red needles, decomposes when dried at 100°, and when reduced with stannous chloride and hydrochloric acid yields sulphuric acid, ammonia, aniline, and *p*-phenylenediamine. When treated with sulphuric acid and sodium nitrite in alcoholic solution, it forms the *substance* $N_2Ph \cdot C_6H_4 \cdot N_3$, which crystallises in small, bronze leaflets and melts at 90—91°. The *potassium* salt, $C_{12}H_{11}O_3N_4SK$, forms reddish-yellow crystals, dissolves in water forming a yellow solution which becomes red on addition of mineral acids, but not of carbon dioxide or hydrogen sulphide, and when oxidised with mercuric oxide yields the *potassium* salt, $N_2Ph \cdot C_6H_4 \cdot N_2 \cdot SO_3K$, from which it is again formed by reduction with ammonium sulphide. The colourless *sulphonic acid*, $C_{12}H_{10}O_3N_4S$, forms stable *barium*, *calcium*, and *silver* salts. G. Y.

Azo-dye from 3:4-Dichloroaniline. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 160788).—The diazonium compound of 3:4-dichloroaniline combines with sodium β -naphthol-3:6-disulphonate to yield a red azo-dye, which forms sparingly soluble metallic lakes remarkably stable towards light. The lakes of the corresponding azo-compounds from 2:4- and 2:5-dichloroanilines are so unstable towards light as to be practically useless. C. H. D.

Yellow Disazo-dyes. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 160674 and 160675).—The tetra-azotised solutions of benzidine-2:2'-disulphonic and 3:3'-tolidine-2:2'-disulphonic acids combine with 2 mols. of 1-phenyl-3-methyl-5-pyrazolone to form yellow *disazo-compounds* which dye wool. Similar dyes are obtained when the same tetra-azo-compounds are combined with 2 mols. of methylindole or with 1 mol. of methylindole and 1 mol. of 1-phenyl-3-methyl-5-pyrazolone. C. H. D.

o-Hydroxyazo-dyes. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 160536. Compare Abstr., 1905, i, 250).—The formation of diazosulphonates in the treatment of diazotised α - and β -naphthyl-aminedi- or poly-sulphonic acids with alkali acetates or carbonates is avoided by adding chlorine or alkali hypochlorites as well as the salt used to fix the acid, thus destroying any sulphites formed. Thus, a diazotised solution of β -naphthylamine-1:5-disulphonate is neutralised with sodium carbonate and an alkaline solution of sodium hypochlorite added. The temperature may rise to 35°. Combination with β -naphthol then takes place in the usual manner. C. H. D.

Hydrolysis of Egg-albumin. A. ADENSAMER and PH. HOERNES (*Monatsh.*, 1905, **26**, 1217—1230. Compare Skraup, Abstr., 1904, i, 954).—Using Skraup's method, the authors have isolated from the products of the hydrolysis of egg-albumin, *d*-alanine, leucine, aminovaleric acid, and a mixture of substances which crystallises in microscopic plates or needles, melts in a sealed capillary tube at 280°, has $[\alpha]_D + 30.196^\circ$, and contains probably aminovaleric acid and *isoleucine*; it forms a copper salt which is readily soluble in methyl alcohol.

The copper salts obtained from the filtrate from the phosphotungstates were fractionally crystallised and made alkaline. The liberated ammonia was removed by distillation in a vacuum and the residue shaken with naphthalene- β -sulphonic chloride, when the only product obtained was naphthalene- β -sulphonamide.

No glycine, pyrrolidine-2-carboxylic, caseanic, or caseic acids could be detected amongst the products of hydrolysis, and if present they must be so only in extremely small quantities. G. Y.

Colloidal Solutions. The Globulins. WILLIAM B. HARDY (*J. Physiol.*, 1905, **33**, 251—337. Compare Abstr., 1903, ii, 469).—This paper deals with the behaviour of globulins to acids, alkalis, and salts, and the properties of the solutions considered as cases of colloidal solution. Globulins are amphoteric electrolytes; the globulin salts ionise in solution, therefore in an electric field the entire mass of proteid

moves. A method for the direct measurement of the specific velocity of globulin ions is described. Among the many other points raised, for which the original paper must be consulted, the complete absence of "ionic" globulin from blood serum is noted. It is probable that the globulin is formed in serum by the decomposition of a more complex proteid.

W. D. H.

Globulins. J. MELLANBY (*J. Physiol.*, 1905, 33, 335—373).—Solution of globulin by a neutral salt is due to forces exerted by its free ions. Ions with equal valencies, whether positive or negative, are equally efficient, and the efficiencies of ions of different valencies are directly proportional to the squares of their valencies. The amount of globulin dissolved by a given percentage of neutral salt is directly proportional to the strength of the original globulin suspension. The precipitation of globulin by neutral salts depends on a molecular combination between the salt and globulin, the compound so formed being stable only in excess of the combining salt. Precipitation by salts of the heavy metals depends on the formation of a stable compound. Solution of globulin by acids or alkalis is of the nature of chemical combination. The relative solvent efficiencies of acids or alkalis are of the same order as their chemical avidities.

W. D. H.

The Group of Organic Acids containing Nitrogen and Sulphur which is present in Normal Human Urine. STANISLAUS BONDZYŃSKI, ST. DOMBROWSKI, and KAZIMIERZ PANEK (*Zeit. physiol. Chem.*, 1905, 46, 83—124. Compare Abstr., 1898, i, 501; 1902, i, 847).—*allo*Oxyproteic acid is precipitated by the addition of lead acetate, and the excess of lead removed by means of sodium carbonate. The addition of mercuric acetate and acetic acid precipitates a new acid, *antioxyproteic acid*, in the form of its *mercuric* salt, and when the filtrate from this is neutralised with sodium carbonate a precipitate of the mercury salt of oxyproteic acid is obtained. The *barium* and *silver* salts of the new acid have been analysed, and the values calculated therefrom for the acid are C 43·21, H 4·91, N 24·4, S 0·61, and O 26·33 per cent. It gives a precipitate with phosphotungstic acid which is soluble in an excess or in water, and from this precipitate the barium salt may be obtained without precipitation with mercuric acetate. The *sodium* and *potassium* salts dissolve readily in water and yield emulsions with alcohol. The alkali-earth salts also dissolve readily in water, but are precipitated as white powders on the addition of alcohol. The acid is dextrorotatory. It gives neither the biuret nor the Millon reaction, but gives both Ehrlich's and Friedenwald's diazo-reactions.

To obtain a good yield of oxyproteic acid, it is advisable to remove the acetic acid and acetates before precipitating *antioxy*- and *oxy*-proteic acids with mercuric acetate; if, however, the pure *antioxyproteic* acid is required, the removal of the acetates is not recommended, as when these are absent a considerable quantity of the oxyproteic acid is precipitated with the *antioxy*-acid. Oxyproteic acid has the composition C 39·62, H 5·64, N 18·08, S 1·12, and O 35·54 per cent.

The acid previously described as *allooxyproteic acid* was not pure, as acids free from sulphur and nitrogen are removed when the colourless mercuric salt is decomposed with hydrogen sulphide and extracted with ether. The composition of the pure *allo-acid* is C 41.33, H 5.70, N 13.55, S 2.19, and O 37.23 per cent. The salts are less soluble in alcohol than those of the other oxyproteic acids. These salts are often coloured by a substance which is comparatively rich in sulphur, and appears to be identical with urochrome.

Thiele's uroferic acid (Abstr., 1904, i, 452) closely resembles, but does not appear to be identical with, *allooxyproteic acid*. J. J. S.

Action of Lactic Acid on Casein and Paracasein. O. LAXA (*Milchw. Zentr.*, 1905, 1, 538—547).—Casein combines with lactic acid to form a number of lactates. The latter are soluble in water, except those which contain less than 1 per cent. of lactic acid. By dialysis, a lactate containing from 1.4 to 1.9 per cent. of lactic acid is produced, whilst by "salting out" a solution of casein in lactic acid, a lactate with 7.5 per cent. of acid is obtained. To term the insoluble lactates "mono-lactates" and the soluble lactates "di-lactates" is therefore inconclusive. The casein lactates contain a proportionately small percentage of phosphorus, from 0.45 to 0.48 per cent. The lactic acid produced by bacteria in the milk converts the phosphates present into acid phosphates and at the same time combines with the casein, forming soluble and insoluble lactates. The soluble lactates, however, are precipitated subsequently by the mineral salts present, and the whole milk curdles. Impregnation of casein with calcium lactate renders the former exceedingly plastic. Paracasein is very probably a compound of casein with calcium phosphates. Acids convert it into casein and it yields the same lactates as casein.

W. P. S.

Amount of Glycine and Alanine from Casein. ZDENKO H. SKRAUP (*Monatsh.*, 1905, 26, 1343—1349. Compare Abstr., 1905, i, 619).—Details are given of the method by which *D*-alanine and glycine have been obtained from casein.

It is considered that the composition of casein varies, and that the appearance of glycine amongst the products of the hydrolysis of commercial casein purified by Hammarsten's method is not due to the presence of an impurity. G. Y.

Kyrines. ZDENKO H. SKRAUP and RUDOLF ZWERGER (*Monatsh.*, 1905, 26, 1403—1414. Compare Skraup, Abstr., 1905, i, 398; Siegfried, Abstr., 1903, i, 586; 1905, i, 104).—When casein is heated on the water-bath for one hour with an equal weight of concentrated hydrochloric acid, the mixture dissolves completely in an equal volume of water, and if the resulting solution is further heated its laevo-rotatory power changes to dextro-rotatory, becoming constant in about forty-eight hours; at the same time, the behaviour of the solution to phosphotungstic acid changes, the precipitates formed at first are resinous, but those obtained after about forty-two hours' heating on the water-bath consist of short prisms and contain nitrogen

and carbon in the atomic proportion 1:2.6, which was found by Siegfried for his caseinokyryne. The basic syrup obtained on treatment of the crystalline phosphotungstate with baryta forms a double salt with cadmium iodide, containing nitrogen and carbon in the atomic proportion 1:2.6, a double salt with potassium iodide, containing nitrogen and carbon in the atomic proportion 1:2.4, and a derivative with naphthalene- β -sulphonic chloride, in which the proportion is 1:2.2. The basic syrup (30 grams) yields 21 grams of lysine picrate, 0.5 gram of arginine nitrate, and 1.5 grams of crude histidine, from which 0.2 gram of the crystalline hydrochloride is obtained. G. Y.

Gelatin. II. ZDENKO H. SKRAUP and F. HECKEL (*Monatsh.*, 1905, 26, 1351—1358. Compare Abstr., 1905, i, 398, 619).—Gelatin was hydrolysed by heating with hydrochloric acid and the product evaporated in a vacuum and esterified by treatment with absolute alcohol and hydrogen chloride. After removal of ethyl aminoacetate hydrochloride, the filtrate was extracted with ether and the residual solution precipitated with phosphotungstic acid in three fractions. The final filtrate, after removal of the phosphotungstic acid, yielded a small amount of glutamic acid. The second phosphotungstate precipitate yielded lysine and arginine. The third precipitate was crystallised from water, when three fractions were obtained; the least soluble part yielded an uncrystallisable syrup; the moderately soluble fraction yielded a mixture of *d*-alanine and glycine, whilst the most soluble part yielded almost pure glycine.

d-Alanine and glycine are separated by repeated fractional crystallisation, alternately, of the copper salts and of the acids. G. Y.

Jecorin. J. MEINERTZ (*Zeit. physiol. Chem.*, 1905, 46, 376—382).—Manasse states that Drechsel's jecorin yields on decomposition the same products as lecithin, with dextrose in addition. Bing regards it as a mixture of various compounds of lecithin, of which lecithin-dextrose is an abundant one. In the present research, jecorin was prepared from liver by Drechsel's method, treated with dilute hydrochloric acid, and dialysed; the dialysable substances are the reducing substance, a nitrogenous material, and inorganic matter containing calcium and phosphoric acid; the residue was without reducing action and showed all the properties of lecithin. W. D. H.

The Chromogen of the so-called Scatole-red contained in Normal Human Urine. J. PH. STAAL (*Zeit. physiol. Chem.*, 1905, 46, 236—262).—Normal human urine, when mixed with hydrochloric acid and a few drops of potassium nitrite solution, yields, in addition to indigo-red, a dye which is insoluble in chloroform and differs spectroscopically from indigo-red. A close examination of this dye proves it to be identical with Nencki and Sieber's uroosein (Abstr., 1883, 101). The chromogen which gives rise to this dye may be extracted by Stokvis' method (*Med. Tijdsch. Gen.*, 1901, i, 961). The ethyl acetate extract may be freed from indican by shaking with water, and when mixed with magnesium carbonate yields a *magnesium* derivative, which may be isolated by removing the ethyl acetate and extracting the

residue with 90 per cent. alcohol. It is a brownish-yellow, amorphous powder, soluble in water, alcohol, acids, or alkalis, but insoluble in ether, chloroform, or acetone. With hydrochloric acid and a few drops of potassium nitrite solution, it yields the stable red dye, which may be extracted with amyl alcohol.

The composition of the magnesium compound is Mg 10.26, C 46.59, H 4.98, and N 3.35 per cent. It is not a "coupled" sulphuric or glycuronic acid, and is not a scatole derivative, as this base is not formed when the compound is reduced, distilled, or fermented by bacteria. When heated with sulphuric acid, it yields acetic and hippuric acids. J. J. S.

Preparation and Analysis of Nucleic Acids. XI. Nucleic Acid from the Mammary Glands of the Cow. JOHN A. MANDEL and PHOEBUS A. LEVENE (*Zeit. physiol. Chem.*, 1905, **46**, 155—158. Compare Abstr., 1900, i, 572; 1901, i, 299, 623; 1902, i, 668, 779; 1904, i, 126; 1905, i, 105, 847).—The copper salt of the nucleic acid gave the following analytical data: C=31.34, H=4.07, N=14.65, P=8.48, Cu=7.00 per cent. When hydrolysed with 2 per cent. sulphuric acid, 100 grams yield guanine 1.05 and adenine picrate 4.56 grams. With 25 per cent. sulphuric acid, thymine, 5 grams, and cytosine picrate, 10 grams, are obtained.

When distilled with hydrochloric acid, the acid yields furfuraldehyde, and with concentrated sulphuric acid, lævulic acid. J. J. S.

Nucleic Acids of the Thymus. III. HERMANN STEUDEL (*Zeit. physiol. Chem.*, 1905, **46**, 332—336. Compare Abstr., 1904, i, 837).—When hydrolysed with acids, nucleic acid yields both purine and pyrimidine bases among other substances. The relationship between these is doubtful. If a reducing agent is added to the acid used in hydrolysis, much of the purine bases is destroyed, but there is no corresponding increase in the pyrimidine bases. If the hydrolysis is carried out with sulphuric acid so energetically as to destroy all the purine bases, the same negative result regarding pyrimidine bases is obtained. Cytosine and thymine are present, but in smaller amount than in experiments where the hydrolysis was not carried so far.

W. D. H.

Catalysis and Enzyme Action. C. HUGH NEILSON (*Amer. J. Physiol.*, 1906, **15**, 148—152).—Further evidence is adduced which shows the similarity between the action of enzymes and that of metallic catalysts. Platinum black and manganese dioxide act in the same way on salicin and amygdalin as emulsin does.

W. D. H.

Physico-chemical Nature and Activity of Enzymes. LUIGI MARINO and G. SERICANO (*Gazzetta*, 1905, **35**, ii, 407—417).—The authors have prepared carefully purified specimens of emulsin and maltase, which were white and dissolved in water giving solutions having a faint reddish-yellow or brownish-red colour, according to the concentration. If a drop of a very concentrated solution of emulsin

is added to a very large quantity of water, the latter becomes milky, but as more emulsin is added the amount remaining in solution gradually increases. The authors compare this phenomenon with that observed with readily hydrolysable inorganic salts. The deposited emulsin has the same composition as that in solution, and exhibits similar behaviour. At temperatures above about 30°, the emulsin solutions remain clear, however great the quantity of added water may be. Maltase exhibits similar comportment, but the temperature above which its solutions remain clear on dilution with water is lower than with emulsin.

Emulsin has the following percentage composition: carbon, 43.68; hydrogen, 7.62; and nitrogen, 13.64, that of maltase being: carbon, 43.48; hydrogen, 6.87; and nitrogen, 6.80.

On exposing an 18—20 per cent. emulsin solution to the action of sunlight in absence of oxygen, it was found that the activity of the enzyme decreased and increased in a periodic manner. The following are the relative amounts of salicin decomposed by a constant quantity of the emulsin solution after exposure to sunlight for different periods: at first, 93.6; after six days, 70.2; after eleven days, 15.1; after sixteen days, 28.0; after twenty-one days, 35.0; after twenty-six days, 38.5; and after sixty days, less than 10.6. After such exposure to sunlight, the emulsin has the same chemical composition and the same physical properties as the original enzyme. Emulsin solutions exposed to only the heat rays or only the light rays of the sunlight underwent no change. The weak sunlight of the end of October exerts no influence on the activity of emulsin solutions.

Maltase exhibits the same behaviour as emulsin when its solutions are acted on by sunlight. Solutions of emulsin and maltase of equal concentration have the same refractive index, specific rotatory power, and specific conductivity.

T. H. P.

Studies on Enzyme Action. Lipase. HENRY E. ARMSTRONG (*Proc. Roy. Soc.*, 1905, *B* 76, 606—608).—In the experiments on castor oil, ground castor oil seed was employed; in the experiments on other esters, the oil was first removed by means of ether.

The observations of Connstein and his co-workers, that ricinus lipase is effective only in presence of acid, and that it acts preferentially on the natural fats, are confirmed. Ethyl mandelate is not much affected by ricinus lipase, whereas it is readily attacked by animal lipase (compare Dakin, *Abstr.*, 1904, i, 1071).

Attempts to prepare an extract containing an enzyme were unsuccessful. When the material, free from fat, is digested with the amount of sulphuric acid in presence of which hydrolysis of fatty oil is rapidly effected, the enzyme is destroyed.

G. S.

Nuclease. FRITZ SACHS (*Zeit. physiol. Chem.*, 1905, 46, 337—353).—The experiments recorded support the theory that ferments exist which are capable of cleaving nuclein with the liberation of nuclein bases. Such ferments are found in the extracts of many tissues, but especial attention is directed in the present research to the nuclease of the pancreatic juice; this is not identical with trypsin, but is destroyed by tryptic action.

W. D. H.

Papain-digestion. FRIEDRICH KUTSCHER and LOHMANN (*Zeit. physiol. Chem.*, 1905, **46**, 383—386).—Contrary to Mendel's statement (Abstr., 1901, i, 355), it is found that abundant quantities of crystalline cleavage products are obtained by the action of papain on proteids. They resemble those obtained by the use of trypsin. Tetra- and penta-methylenediamines, which are characteristic of the prolonged action of pepsin, could not be prepared. W. D. H.

Action of Rennin. I. H. REICHEL and KARL SPIRO (*Beitr. chem. Physiol. Path.*, 1905, **7**, 485—507).—The experiments relate mainly to reaction velocity and show that within quite wide limits the amount of enzyme and the time of curdling are inversely proportional. The influence of calcium salts follows an equally simple law. The effect of other substances was also studied. W. D. H.

Ferment Action and Ferment Loss. II. H. REICHEL and KARL SPIRO (*Beitr. chem. Physiol. Path.*, 1905, **7**, 479—484. Compare Abstr., 1904, i, 1071).—In milk, the loss of the enzyme rennin is related to the amount of calcium salts present. In specimens containing such salts, the loss increases, and in those in which the calcium percentage is kept constant the amount lost rises with higher concentrations of rennin, and is relatively greater than in those poor in calcium salts. Magnesium chloride acts in a similar way, but not so markedly. Potassium thiocyanate increases the loss slightly; glycerol and urea increase it greatly, but possibly in some cases an injurious effect on the ferment has here to be dealt with, and not merely a division of the amount of ferment between curd and whey. W. D. H.

Studies on Enzyme Action. VII. **The Synthetic Action of Acids contrasted with that of Enzymes.** **Synthesis of Maltose and isoMaltose.** E. FRANKLAND ARMSTRONG (*Proc. Roy. Soc.*, 1905, **B 76**, 592—599. Compare Trans., 1903, **83**, 1305; Abstr., 1904, i, 956—958, 1070; 1905, i, 746).—When dextrose is condensed by means of hydrochloric acid (compare Fischer, Abstr., 1891, 412; 1896, 119), both maltose and its isomeride *isomaltose* are produced. To detect *isomaltose*, the acid was removed by means of lead carbonate and the filtered solution fermented with *Saccharomyces intermedians* to get rid of unaltered dextrose; from the resulting solution, an osazone was obtained which behaved in all respects like the osazone of *isomaltose* obtained by E. Fischer. In testing for maltose, the dextrose was removed from another portion of the solution by fermenting with *S. Marxiana*, which contains no maltase, and the maltose confirmed by observing the rotatory power of the solution, by preparation of the osazone, and by its behaviour towards maltase.

Dextrose was also condensed by means of maltase and emulsin. In the former case, *isomaltose* was produced, but the solution was not tested for maltose; with emulsin, maltose was formed, but probably not *isomaltose*. The investigation of these points is being continued.

The theory of condensation by acids and enzymes is discussed.

With acids, both isomerides are to be expected, since the condensation is "uncontrolled," but with enzymes, owing to their selective action, the process is probably controlled. Experiment shows, as in the above examples, that an enzyme favours the production of a sugar isomeric with that which it can hydrolyse; the question as to how the control of the enzyme is exerted so as to produce this result is considered.

G. S.

Studies on Enzyme Action. VIII. The Mechanism of Fermentation. E. FRANKLAND ARMSTRONG (*Proc. Roy. Soc.*, 1905, *B* 76, 600—605. Compare preceding abstract).—The action of twenty typical pure yeasts, prepared by Hansen's methods, on dextrose, mannose, lævulose, and galactose has been investigated. Whereas the three first-mentioned sugars were fermented, apparently with equal readiness, by all the yeasts, about half of the latter had no action on galactose, a result which is in accordance with previous observations. This inability to ferment galactose has nothing to do with the absence of hydrolysing enzymes, since it was observed with yeasts containing invertase, maltase, and lactase respectively. Further, dextrose, mannose, and lævulose were readily fermented by yeasts which do not contain any enzyme capable of inducing the hydrolysis of bioses. From these results, it is clear that the processes of enzymo-hydrolysis and of fermentation differ in some essential respects, although, for reasons given in a previous paper (*Abstr.*, 1904, *i*, 957), it is probable that they are cognate phenomena.

It is pointed out that the three hexoses which behave alike have a common enolic form and the change to this is probably the initial stage in fermentation. The mechanism of the fermentation of galactose seems to be different from that of the other three sugars.

G. S.

Diphenylsilicone and Benzylsilicon Compounds. WALTHER DILTHEY [and FRITZ EDUARDOFF] (*Ber.*, 1905, 38, 4132—4136. Compare *Abstr.*, 1904, *i*, 132, 464).—The gelatinous diphenylsilicone (diphenyl silicoketone) becomes crystalline when rubbed with a few drops of acetic anhydride. It separates from chloroform and light petroleum in clear, flat prisms melting at 188° and readily soluble in ether, benzene, or chloroform. Both the gelatinous and the crystalline compounds are trimolecular, probably $O \begin{smallmatrix} \diagup SiPh_2 \cdot O \\ \diagdown SiPh_2 \cdot O \end{smallmatrix} SiPh_2$.

Dibenzylsilicol, $Si(CH_2Ph)_2(OH)_2$, crystallises from a mixture of benzene and light petroleum, melts at 76°, and dissolves readily in ether, benzene, or chloroform. The yield is small. *Tribenzylsilicol*, $Si(CH_2Ph)_3 \cdot OH$, is obtained when a larger quantity of magnesium benzyl chloride is used; it crystallises from alcohol in long, colourless needles and melts at 106°.

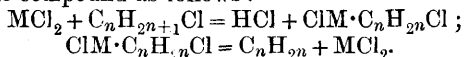
J. J. S.

Organic Chemistry.

New Isomeride of Heptane: *s*-Tetramethylpropane [$\beta\delta$ -Dimethylpentane]. MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 910—911).—For $\beta\delta$ -dimethylpentane (compare Chonin, Abstr., 1905, i, 729), the author gives the following constants: boiling point, 83—84° under 749 mm. pressure; sp. gr. 0.7022 at 0°/0° and 0.6879 at 22°/0°; n_D 1.38477 at 22°.

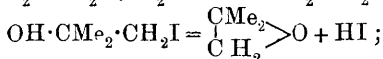
T. H. P.

New Method of Preparing Olefines. ALPHONSE MAILHE (*Chem. Zeit.*, 1906, 30, 37).—When the monohalogen substituted paraffins are passed through a glass tube containing reduced nickel, cobalt, or copper heated at 250° or more, they are decomposed into the corresponding halogen acid and an olefine; these two substances are prevented from recombining by passing through potassium hydroxide solution. The chloro-derivatives are decomposed below 250°, whilst the bromo- and iodo-derivatives require increasingly higher temperatures; ethyl iodide, for example, is only decomposed at a temperature of 360°. The dried chlorides of the bivalent metals nickel, cobalt, cadmium, iron, lead, barium, &c., also act catalytically in the same way at about 300°, barium chloride being most efficient. In the case of the bromo-derivatives, a slightly higher temperature, about 320°, is necessary, and, owing to the greater tendency of the decomposition products to reunite, the yield of hydrocarbon is not so good. The anhydrous bromides of lead, cadmium, nickel, or barium and the iodides of lead or cadmium have been found to act in a similar manner at 320°. Since the halogen derivatives of univalent metals are not able to effect this decomposition, it is assumed that the reaction entails the intermediate formation of an organo-metallic compound as follows:

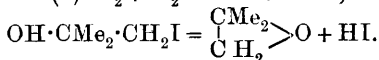


P. H.

Reaction of Iodine with *iso*Butylene. S. A. POGORZELSKY (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 814—818. Compare Abstr., 1905, i, 165, 315).—The action of *isobutylene* on iodine in potassium iodide solution yields mainly trimethylcarbinol and *isobutylene* α -oxide, together with a small quantity of *tert.*-butyl alcohol. The author regards the reaction as expressed by either: (1) $\text{CMe}_2\text{:CH}_2 + \text{I}_2 = \text{CMe}_2\text{I} \cdot \text{CH}_2\text{I}$; $\text{CMe}_2\text{I} \cdot \text{CH}_2\text{I} + \text{H}_2\text{O} = \text{OH} \cdot \text{CMe}_2 \cdot \text{CH}_2\text{I} + \text{HI}$;



or (2) $\text{I}_2 + \text{H}_2\text{O} = \text{HI} + \text{HIO}$; $\text{CMe}_2\text{:CH}_2 + \text{HIO} = \text{OH} \cdot \text{CMe}_2 \cdot \text{CH}_2\text{I}$;



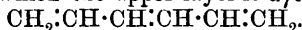
T. H. P.

Combustion of Acetylene in Oxygen. PAUL MAURICHEAU-BEAUPRÉ (*Compt. rend.*, 1906, 142, 165—166).—In addition to carbon

dioxide and water vapour, the gaseous products of the oxyacetylene blowpipe flame contain oxides of nitrogen and ozone (compare Berthelot, Abstr., 1900, ii, 475, 538); after removing the oxides of nitrogen by means of ferrous sulphate crystals moistened with concentrated potassium carbonate solution (compare Gautier, Abstr., 1898, ii, 537), the amount of carbon monoxide in the residual gaseous mixture was determined by the method of Albert-Lévy and Pecoul (Abstr., 1905, ii, 203) and found to be less than 1 in 100,000.

M. A. W.

The Simplest Hydrocarbon with Two Conjugated Systems of Double Bonds. *αγ*-Hexatriene. PIETER VAN ROMBURGH and W. VAN DORSSEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 565—568. Compare this vol., i, 141).—When slowly heated at 165°, and then gradually to 200°, the diformate of *s*-divinyl glycol, or a mixture of the diformate with the glycol, evolves carbon dioxide and a small amount of carbon monoxide, and yields a distillate consisting of two layers, of which the upper layer is *αγ*-hexatriene,



This is a colourless, strongly refracting liquid, which boils at 78·5—80° (corr.) under 766 mm. pressure and has the sp. gr. 0·7565 at 10° and $n_D = 1\cdot49856$ at 10°; it is reduced by sodium and boiling absolute alcohol, and is oxidised slowly when exposed to the air. It forms a *dibromide* melting at 89—90°, and a *tetrabromide* melting at 115°.

G. Y.

Conditions under which the Metal-ammonium Compounds reduce Halogen Derivatives of the Fatty Hydrocarbons. Preparation of Olefines and Paraffins. E. CHABLAY (*Compt. rend.*, 1906, 142, 93—95. Compare Abstr., 1905, i, 502; Lebeau, Abstr., 1905, i, 401, 512).—Ethylene dichloride reacts with sodammonium to form ethylene, sodium chloride, and ammonia, according to the equation $\text{C}_2\text{H}_4\text{Cl}_2 + 2\text{NaNH}_3 = 2\text{NaCl} + \text{C}_2\text{H}_4 + 2\text{NH}_3$, and similar results were obtained when the dibromides of propylene, pseudobutylene, isobutylene, or trimethylene replaced the ethylene dichloride in the above reaction. The dichloride of methylene, ethylidene, or propylidene or $\beta\beta$ -dichloropropane yields the corresponding paraffin (methane, ethane, or propane) by the action of sodammonium.

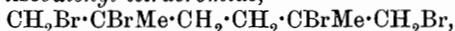
M. A. W.

Pyrogenic Behaviour of Tetrachloroethylene, Acetyl Chloride, Trichloroacetic Acid, and Bromoform. MATTHIAS JOIST and WALTHER LÖB (*Zeit. Elektrochem.*, 1905, 11, 938—944).—Experiments made in the way described previously (Abstr., 1902, i, 3) show that tetrachloroethylene yields hexachlorobenzene and hexachloroethane. The decomposition of acetyl chloride is represented by the equation $2\text{CH}_3\cdot\text{COCl} = 2\text{HCl} + 2\text{CO} + \text{C}_2\text{H}_4$. Bromoform yields tetrabromoethylene and bromine, whilst in presence of water formic acid is also produced. The reactions are explained as before by the intermediate formation of CCl_2 , CBr_2 , and similar unsaturated substances.

Trichloroacetic acid is entirely broken up, thus: $2\text{CCl}_3\cdot\text{CO}_2\text{H} + \text{H}_2\text{O} = 3\text{CO} + \text{CO}_2 + 4\text{HCl} + \text{Cl}_2$.

T. E.

Diisobutenyl Tetrabromide [$\alpha\beta\epsilon\zeta$ -Tetrabromo- $\beta\epsilon$ -dimethylhexane]. S. A. POGORŽELSKY (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 809—814).—*Diisobutenyl tetrabromide*,



separates from ether in monoclinic crystals [$a:b:c=1.2412:1:1.2318$; $\beta=118^\circ56'5''$] melting at 100° . T. H. P.

Etherates of Haloid Compounds of Magnesium. II. Action of Anhydrous Alcohols on Etherates of Magnesium Bromide; Crystalline Alcoholates of Magnesium Bromide. BORIS N. MENSCHUTKIN (Reprint from *Bull. St. Petersburg Polytechnic Inst.*, 1905, 3, 29 pp. Compare Abstr., 1904, i, 215).—The etherates of magnesium bromide and iodide react readily with organic compounds of various kinds, such as alcohols, acids, aldehydes, ketones, and ethers. On dissolving $\text{MgBr}_2\cdot\text{Et}_2\text{O}$ in a slight excess of an alcohol, heat is developed and the ether is replaced by the alcohol forming a compound of the type $\text{MgBr}_2\cdot6\text{R}\cdot\text{OH}$. These compounds are colourless, hygroscopic, and slightly soluble in water. Each of them can be crystallised from the alcohol it contains, the readiness of crystallisation falling off continuously as the molecular weight increases. The melting points of the compounds formed with methyl, ethyl, propyl, isobutyl, and isomyl alcohols are given below, together with those of the corresponding alcohols:

MeOH	— 94°	$\text{MgBr}_2\cdot6\text{MeOH}$	190°
EtOH	— 112	$\text{MgBr}_2\cdot6\text{EtOH}$	108.5°
PrOH	— 127	$\text{MgBr}_2\cdot6\text{PrOH}$	52
$\text{C}_4\text{H}_9\cdot\text{OH}$	— 108	$\text{MgBr}_2\cdot6\text{C}_4\text{H}_9\cdot\text{OH}$	80
$\text{C}_5\text{H}_{11}\cdot\text{OH}$	— 117.2°	$\text{MgBr}_2\cdot6\text{C}_5\text{H}_{11}\cdot\text{OH}$	46

The solubilities of the separate compounds in the corresponding alcohols at different temperatures are given in the form both of tables and curves. T. H. P.

Etherates of Haloid Compounds of Magnesium. III. Action of Anhydrous Alcohols on Etherates of Magnesium Iodide; Crystalline Alcoholates of Magnesium Iodide. BORIS N. MENSCHUTKIN (Reprint from *Bull. St. Petersburg Polytechnic Inst.*, 1905, 3, 12 pp. Compare preceding abstract).—Crystalline alcoholates of magnesium iodide can be prepared by a method analogous to that employed for the corresponding magnesium bromide compounds (*loc. cit.*). The ethylate of magnesium iodide crystallises in six-sided plates, 8—9 mm. in length, and rapidly turns yellow in the air. The melting points of the compounds prepared by the author are as follows: $\text{MgI}_2\cdot6\text{MeOH}$, above 210° ; $\text{MgI}_2\cdot6\text{EtOH}$, 146.5° ; $\text{MgI}_2\cdot6\text{PrOH}$, $65\text{—}70^\circ$; $\text{MgI}_2\cdot6\text{C}_4\text{H}_9\cdot\text{OH}$ (*iso*), $95\text{—}100^\circ$; $\text{MgI}_2\cdot6\text{C}_5\text{H}_{11}\cdot\text{OH}$ (*iso*) could not be obtained in a crystalline form. The solubilities of the methylate in methyl alcohol and that of the ethylate in ethyl alcohol have been determined at various temperatures. T. H. P.

Etherates of Haloid Compounds of Magnesium. IV. Action of Water on the Etherates; Solubility of Hydrates of Magnesium Bromide and Iodide in Water. BORIS N. MENSCHUTKIN (Reprint from *Bull. St. Petersburg Polytechnic Inst.*, 1905, 4, 26 pp. Compare preceding abstracts).—The action of small quantities of water on etherates of magnesium bromide and iodide at moderately high temperatures (35–40°) yields etherates of hydroxyhaloid compounds of magnesium. With larger quantities of water, acting at the ordinary temperature, the hexahydrate of magnesium bromide and the octahydrate of magnesium iodide are obtained.

The etherate of magnesium hydroxybromide,
 $\text{MgBr}\cdot\text{OH}, \text{MgBr}_2\cdot 2\text{Et}_2\text{O}$,
 has already been prepared by Holroyd (*Proc.*, 1904, 20, 38). The etherate of magnesium hydroxyiodide, $\text{MgI}\cdot\text{OH}, 2\text{Et}_2\text{O}$, is obtained as a hygroscopic, unstable, white powder.

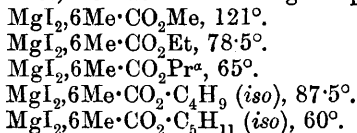
Magnesium bromide hexahydrate melts at 164° and its solubility in water has been determined from –5° to 164°. The solubility of magnesium iodide octahydrate, melting at 43·5°, has been measured from 0° to 43°, at which temperature it is converted into the hexahydrate, decomposing at above 200°; the solubility curve for the hexahydrate is given for the range of temperature 43–200°.

The solubility curves of hexahydrated magnesium bromide and iodide in water and of the crystalline methyl and ethyl alcoholates of magnesium bromide and iodide in methyl and ethyl alcohols are, in general, of the same type. The curve for $\text{MgBr}_2\cdot 6\text{MeOH}$ in methyl alcohol, however, although similar to the other curves, does not lie between that for $\text{MgBr}_2\cdot 6\text{H}_2\text{O}$ in water and that for $\text{MgBr}_2\cdot 6\text{EtOH}$ in ethyl alcohol; this depends on the divergence in character of methyl alcohol from its homologues.

T. H. P.

Etherates of Haloid Compounds of Magnesium. V. Action of Esters: Compounds of Magnesium Iodide and Bromide with Esters. BORIS N. MENSCHUTKIN (Reprint from *Bull. St. Petersburg Polytechnic Inst.*, 1905, 4, 37 pp. Compare preceding abstracts and *Abstr.*, 1904, i, 215).—With many esters, magnesium iodide and bromide form compounds, which in many cases crystallise well.

The compounds of magnesium iodide with acetic esters, which are well-crystallised substances, melt at the following temperatures:



The alternate fall and rise of the melting point here exhibited finds a very close parallel in the behaviour of the melting points of the corresponding esters of furandicarboxylic acid (see Yoder and Tollens, *Abstr.*, 1902, i, 49. Compare also Arbusoff, *Abstr.*, 1905, i, 316). Solubility curves and tables are given for each of the above magnesium iodide compounds in the particular ester it contains. These compounds are all very hygroscopic and are decomposed by water with liberation of the esters from which they are prepared.

The following compounds have also been prepared : $\text{MgI}_2 \cdot 6\text{H} \cdot \text{CO}_2\text{Et}$, which melts at 70.5° and the solubility of which in ethyl formate has been determined from 0° to 70.5° ; $\text{MgBr}_2 \cdot 2\text{C}_6\text{H}_5 \cdot \text{CO}_2\text{Et}$, melting at about 110° ; $\text{MgBr}_2 \cdot 2\text{C}_6\text{H}_5 \cdot \text{CO}_2\text{C}_4\text{H}_9$, melting at about 130° ;

$\text{MgI}_2 \cdot 3\text{C}_6\text{H}_5 \cdot \text{CO}_2\text{Me}$,
melting at $115\text{--}117^\circ$; $\text{MgI}_2 \cdot 3\text{C}_6\text{H}_5 \cdot \text{CO}_2\text{Et}$, melting at 105° ;

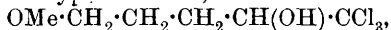
$\text{MgBr}_2 \cdot 2\text{CH}_2(\text{CO}_2\text{Et})_2$,
melting at 135° ; $\text{MgI}_2 \cdot 4\text{CH}_2(\text{CO}_2\text{Et})_2$, melting at 115° and decomposing and resolidifying at $120\text{--}125^\circ$.
T. H. P.

The :C(OH) Group of Tertiary Alcohols. LOUIS HENRY (*Compt. rend.*, 1906, **142**, 129—136).—A theoretical paper in which the author discusses the effect on the :C(OH) group of a tertiary alcohol of introducing negative elements or groups such as Cl, CN, or CO as substituents into the molecule, in respect of its behaviour towards such reagents as hydrochloric acid and acetyl chloride.

M. A. W.

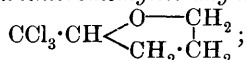
Application of Grignard's Reaction to Ethyl Chloroacetate. E. SÜSSKIND (*Ber.*, 1906, **39**, 225—226).—*Chloromethyldiethylcarbinol*, $\text{CH}_2\text{Cl} \cdot \text{C}(\text{Et})_2 \cdot \text{OH}$, obtained from magnesium ethyl bromide and ethyl chloroacetate, boils at $166\text{--}167^\circ$ under the ordinary pressure and at $70\text{--}72^\circ$ under 18 mm. By interaction with secondary amines, the following compounds have been obtained : *dimethylaminomethyldiethylcarbinol*, boiling at 172° under the ordinary pressure and at $62.5\text{--}63.5^\circ$ under 12.5 mm., *diethylaminomethyldiethylcarbinol*, boiling at $89\text{--}90^\circ$ under 20 mm. pressure, and *piperidinomethyldiethylcarbinol*, boiling at 112° under 15 mm. pressure.
C. S.

€€€-Trichloro- α -methoxypentane- δ -ol and 2-Trichloromethyltetrahydrofuran. JULES HAMONET (*Compt. rend.*, 1906, **142**, 210—211. Compare *Abstr.*, 1904, i, 467, 705; this vol., i, 58).—€€€-Trichloro- α -methoxypentane- δ -ol,



obtained by the action of chloral on the magnesium derivative of α -iodo- γ -methoxypropane, is a colourless solid melting at 59° and boiling at $142\text{--}143^\circ$ under 17 mm. pressure; it has an odour similar to that of camphor and a bitter taste, is insoluble in water, but readily soluble in alcohol, chloroform, or ether, crystallising from the last solvent in monoclinic plates [$a:b:c = 1.008:1:1.75$; $\beta = 108^\circ 25'$]. It does not reduce an alcoholic solution of silver nitrate in the presence of ammonia, but readily reduces Fehling's solution or silver oxide precipitated by an alkali.

An attempt to prepare the corresponding pentene derivative by distilling €€€-trichloro- α -methoxypropane- δ -ol with phosphoric oxide (compare Vitoria, *Abstr.*, 1905, i, 110) was not successful, the product of the reaction being 2-trichloromethyltetrahydrofuran,



it is a colourless, mobile liquid, with a strong odour similar to that of camphor, has a bitter and burning taste, and a sp. gr. 1.42 at 18° ; it

boils at 90—91° under 17 mm. or 203—204° under 758 mm. pressure; it is insoluble in water, but soluble in alcohol or ether. It has no reducing action on alcoholic silver nitrate or on Fehling's solution, and is not readily attacked by alcoholic sodium hydroxide.

M. A. W.

Asymmetric Derivatives of Hexane- α - ζ -diol; Diethyl Ether and Di-iodo-derivative of Heptane- α - η -diol. R. DIONNEAU (*Compt. rend.*, 1906, 142, 91—92).— ζ -Bromo- α -ethoxyhexane, $\text{OEt} \cdot [\text{CH}_2]_6 \cdot \text{Br}$, prepared by the action of hydrobromic acid on α - ζ -diethoxyhexane, has not yet been obtained quite pure, but forms the chief constituent of the fraction boiling between 121° and 123° under 35 mm. pressure. By boiling with sodium iodide in alcoholic solution, it is converted into ζ -iodo- α -ethoxyhexane, $\text{OEt} \cdot [\text{CH}_2]_6 \cdot \text{I}$, a colourless liquid boiling at 138—139° under 35 mm. pressure, and having a sp. gr. 1.379 at 11°/4°. This forms a magnesium derivative, $\text{OEt} \cdot [\text{CH}_2]_6 \cdot \text{MgI}$, which reacts with iodoethoxymethane to form α - η -diethoxyheptane, $\text{OEt} \cdot [\text{CH}_2]_7 \cdot \text{OEt}$ (compare Hamonet, *Abstr.*, 1904, i, 467; 1905, i, 403), a colourless liquid with a fruity odour, boiling at 129° under 35 mm. pressure and having a sp. gr. 0.853 at 11°/4°. α - η -Di-iodoheptane, $\text{C}_7\text{H}_{14}\text{I}_2$, prepared by the action of hydriodic acid in sealed tubes at 100° on the preceding compound, is a stable liquid which boils at 178° under 20 mm. pressure, has a sp. gr. 1.943 at 8°/8°, and solidifies to form colourless crystals melting at about 0°.

M. A. W.

$\alpha\beta\beta$ -Trichloroethyl Ether. GIUSEPPE ODDO and EFISIO MAMELI (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 587—595. Compare *Abstr.*, 1904, i, 280).—The action of 50 per cent. potassium hydroxide solution on $\alpha\beta\beta$ -trichloroethyl ether proceeds much more rapidly than that of water, but yields the same products; the same is the case with the action of an aqueous solution of ethylamine, and with that of saturated sodium hydrogen sulphite solution.

The action of dry ammonia on the ether yields dichloroacetal in quantities varying with the conditions, together with liquids boiling below and above 181—184° and complex resinous substances containing nitrogen.

When heated with magnesium, the ether is only slightly attacked, giving small quantities of substances boiling below and above 170—175°. Also when solvents are present, the magnesium effects but little action, yielding, when benzene is employed, dichloroacetal.

Zinc dust acts more readily on the ether than does magnesium, giving hydrogen chloride, dichloroacetaldehyde, and a voluminous, resinous mass. In presence of ethyl ether, an energetic reaction takes place on heating, but no organo-zinc compound analogous with the organo-magnesium compounds prepared by Grignard is obtained. On treating with water the product of the reaction between zinc and the trichloro-ether in presence of ethyl ether, it yields dichloroacetal, together with small quantities of dichloroacetaldehyde hydrate, of the additive product of dichloroacetaldehyde (1 mol.) with ethoxide (2 mols.), boiling at 110—111°, and of products boiling at above 184°.

Attempts have been made to prepare $\beta\beta$ -dichloroethyl ether by

reducing the trichloro-ether with zinc or magnesium under various conditions, but without success.

Dichloromonothioacetal, $\text{CHCl}_2 \cdot \text{CH}(\text{OEt}) \cdot \text{SEt}$, prepared by the interaction of ethyl mercaptan and $\alpha\beta\beta$ -trichloroethyl ether, was obtained as a yellowish-red liquid boiling at $110\text{--}125^\circ$ under 20—30 mm. pressure.

Phenylethylidichloroacetal, $\text{CHCl}_2 \cdot \text{CH}(\text{OEt}) \cdot \text{OPh}$, prepared by the action of anhydrous sodium phenoxide on $\alpha\beta\beta$ -trichloroethyl ether in benzene solution, is a reddish-brown, unstable liquid, which boils at $165\text{--}170^\circ$ under 40 mm. pressure, dissolves in alcohol, decolorises potassium permanganate, and combines with bromine, giving a white, solid substance.

The interaction of molecular proportions of $\alpha\beta\beta$ -trichloroethyl ether and pyridine in ethereal solution yields an oily, red precipitate, which forms: (1) a *platinichloride*, $(\text{CHCl}_2 \cdot \text{CHCl} \cdot \text{OEt}, \text{C}_5\text{H}_5\text{N})_2, \text{PtCl}_4$, crystallising from dilute hydrochloric acid in mamillary masses of slender, orange-yellow needles melting and decomposing at $208\text{--}209^\circ$; (2) an *aurichloride*, $(\text{CHCl}_2 \cdot \text{CHCl} \cdot \text{OEt}, \text{C}_5\text{H}_5\text{N}), \text{AuCl}_3$, as a heavy, yellow precipitate melting at $92\text{--}93^\circ$. T. H. P.

Liberation of Carbon Monoxide [from Organic Compounds]. AUGUSTIN BISTRZYCKI and B. VON SIEMIRADZKI (*Ber.*, 1906, 39, 51—66).—The following compounds yield carbon monoxide when heated alone or with sulphuric acid, sulphur chloride, phosphorus pentachloride, &c. Quantitative experiments were made on all substances the formulæ of which are given.

I. Formic acid and its methyl and ethyl esters.

II. α -Hydroxy-acids and their derivatives, namely, diphenylene-glycollic acid, $\text{C}_{14}\text{H}_{10}\text{O}_3$; lactic acid, $\text{C}_3\text{H}_6\text{O}_3$; α -methoxyphenylacetic acid, $\text{OMe} \cdot \text{CHPh} \cdot \text{CO}_2\text{H}$; mandelic acid, $\text{C}_8\text{H}_8\text{O}_3$; o -methoxyphenoxy-acetic acid, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$; phenylchloroacetic acid, and α -alanine, $\text{C}_3\text{H}_7\text{O}_2\text{N}$.

III. Oxalic acid and its derivatives: ethyl oxalate and oxamide, $\text{C}_2\text{H}_4\text{O}_2\text{N}_2$.

IV. α -Dicarbonyl compounds: pyruvic acid, $\text{C}_3\text{H}_4\text{O}_3$, and benzoyl-formic acid, $\text{C}_8\text{H}_6\text{O}_3$.

V. Tertiary acids: sulphocamphylic acid, $\text{C}_{10}\text{H}_{16}\text{O}_4$; *m*-chloro-*p*-hydroxytriphenylacetic acid, $\text{C}_{20}\text{H}_{15}\text{O}_3\text{Cl}$; camphoronic acid, $\text{CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CMe}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$;

dimethylmalonic acid, $\text{C}_5\text{H}_8\text{O}_4$; methyl diphenyl-*p*-tolylacetate,

$\text{C}_{22}\text{H}_{20}\text{O}_2$;
p-tolyl diphenylacetolactone, $\text{C}_{21}\text{H}_{16}\text{O}_3$; 3:5-(or 2:4-)dihydroxytritanolactone, $\text{HO} \cdot \text{C}_6\text{H}_3 \langle \text{CPh}_2 \rangle \text{CO}$.

VI. Secondary and primary acids: *p*-hydroxydiphenylacetic acid, $\text{C}_{14}\text{H}_{12}\text{O}_3$; diphenylacetic acid, $\text{C}_{14}\text{H}_{12}\text{O}_2$; and (in small amounts) phenylacetic acid, $\text{C}_8\text{H}_8\text{O}_2$; palmitic acid, $\text{C}_{16}\text{H}_{32}\text{O}_2$.

VII. Ketones and aldehydes: benzaldehyde (small amounts); camphor at 360° ; potassium lævulate (by electrolysis); *p*-tolylpenta-decyl ketone.

m-Chloro-*p*-hydroxytriphenylacetic acid, $\text{CO}_2\text{H}\cdot\text{CPh}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{OH}$, prepared by condensing benzilic acid with *o*-chlorophenol by means of stannic chloride, crystallises from a mixture of benzene and light petroleum in colourless, microscopic tablets and melts at 189° .

Methyl diphenyl-p-tolylacetate (compare Bistrzycki and Wehrbein, Abstr., 1901, i, 712) crystallises from methyl alcohol in long, colourless, microscopic tablets and melts at 135° . T. M. L.

The Capacity of Methoxyl and Ethoxyl Groups for Replacement by [Alkyl] Radicles. Synthesis of Polybasic Acids. SERGIUS N. REFORMATSKY (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 881—889).—In the replacement of alkoxy groups by alkyl radicles by the action of, for instance, an organo-zinc compound on an ester, it is generally assumed that the carbonyl group reacts in the first stage of the change and the alkoxy group in the second, thus: (1) $\text{R}\cdot\text{CO}\cdot\text{OEt} + \text{ZnR}'\text{I} = \text{IZn}\cdot\text{O}\cdot\text{CRR}'\cdot\text{OEt}$; (2) $\text{IZn}\cdot\text{O}\cdot\text{CRR}'\cdot\text{OEt} + \text{ZnR}'\text{I} = \text{CRR}'_2\cdot\text{OZnI} + \text{ZnI}\cdot\text{OEt}$. It has not, however, been shown that the OEt group is not directly replaced by the alkyl radicle, forming $\text{R}\cdot\text{CO}\cdot\text{R}'$, which would then react with $\text{ZnR}'\text{I}$, giving $\text{CRR}'_2\cdot\text{OZnI}$.

The author's attempts to isolate intermediate products formed in reactions similar to the above have as yet yielded no definite results (see this vol., i, 138). T. H. P.

Double Acetates of Gold. Crystallised Barium Auryl Oxide. F. WEIGAND (*Zeit. angew. Chem.*, 1906, 19, 139—140).—The double acetates of gold with calcium, barium, strontium, magnesium, or lead were prepared by adding the hydroxides of these metals to a solution of auric chloride and dissolving the moist precipitates so obtained in boiling glacial acetic acid; the solutions deposited monoclinic crystals of compounds of the following formulæ: $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2, 2\text{Au}(\text{C}_2\text{H}_3\text{O}_2)_3$; $\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2, 2\text{Au}(\text{C}_2\text{H}_3\text{O}_2)_3, 2\text{H}_2\text{O}$; $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2, 2\text{Au}(\text{C}_2\text{H}_3\text{O}_2)_3, 2\text{H}_2\text{O}$; $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2, 2\text{Au}(\text{C}_2\text{H}_3\text{O}_2)_3, 4\text{H}_2\text{O}$; $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2, 2\text{Au}(\text{C}_2\text{H}_3\text{O}_2)_3, 2\text{H}_2\text{O}$. These substances are all soluble in water to give neutral solutions which slowly decompose; when heated on platinum foil, the gold is partially volatilised in the form of red fumes. The filtrate from the precipitate obtained by adding barium hydroxide to the auric chloride solution deposited, after some time, small, yellowish-green, rhombic crystals having the composition $\text{Ba}(\text{O}\cdot\text{AuO})_2, 5\text{H}_2\text{O}$; these dissolve with difficulty in water to give an alkaline solution. P. H.

The Oxidation of Oils. HENRY R. PROCTER and W. E. HOLMES (*J. Soc. Chem. Ind.*, 1905, 24, 1287—1290).—The results of numerous experiments are given in tabular form with the object of elucidating the chemical changes which take place when oils are oxidised by blowing air through them while in a heated condition. Without exception, the sp. gr. and refractive index increased as oxygen was absorbed and the iodine number diminished, but complete saturation was never reached. In some instances, the iodine number remained unaltered during the first three or four hours' blowing, although oxygen was being absorbed, indicating that the oxygen was not

attached to the unsaturated linkings measured by the iodine number. When, however, the iodine number commenced to decrease, it did so rapidly. The oils experimented with comprised liver oils, fish oils, linseed oil, rape oil, cotton-seed oil, olive oil, castor oil, lard oil, &c.

W. P. S.

Pyruvic Acid. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1905, 524—525).—When pyruvic acid is dissolved in sulphuric acid and the solution gently heated, it blackens and carbon monoxide, mixed with a little carbon dioxide, is evolved. Concentrated nitric acid converts it into oxalic acid, but with dilute nitric acid, carbon dioxide and a little formic acid are formed. Pyruvic acid reduces chromic acid, auric chloride, and selenic acid when warmed with their aqueous solutions. At temperatures slightly higher, it reduces mercuric chloride to mercurous chloride and mercurous nitrate to metallic mercury. When warmed with mercuric or silver oxide, some acetic acid is produced. Pyruvic acid reduces uranic sulphate, uranium nitrate, and potassium dichromate. With the last-named, carbon dioxide and some acetic acid are produced.

T. A. H.

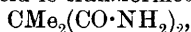
Glycidic Condensation of Aldehydes with Ethyl α -Chloropropionate. GEORGES DARZENS (*Compt. rend.*, 1906, 142, 214—215. Compare this vol., i, 62).—Acetaldehyde, propaldehyde, or *isovaleraldehyde* condense with ethyl α -chloropropionate to form $\alpha\beta$ -disubstituted glycidates of the type $\text{O} \begin{array}{c} \text{CMe} \cdot \text{CO}_2\text{Et} \\ \diagup \quad \diagdown \\ \text{CHR} \end{array}$, but the yield is poor, 20

to 30 per cent. of the theoretical. The aromatic aldehydes readily condense with ethyl α -chloropropionate, and the substituted glycidic acids thus prepared yield ketones of the type $\text{R} \cdot \text{CH}_2 \cdot \text{COMe}$ on distillation; *ethyl β -phenyl- α -methylglycidate* boils at 153—154° under 18 mm. pressure, and the corresponding acid yields carbon dioxide and benzylmethyl ketone on distillation. *Ethyl β -anisyl- α -methylglycidate* boils at 189—190° under 20 mm. pressure, and the aqueous solution of the corresponding sodium salt is decomposed by boiling into sodium hydrogen carbonate and anisyl ketone. *Ethyl β -piperonyl- α -methylglycidate* boils at 205—210° under 25 mm. pressure, and piperonylacetone is obtained by boiling an aqueous solution of the corresponding sodium salt. *Ethyl β -furyl- α -methyl glycidate* is a colourless liquid boiling at 150—151° under 30 mm. pressure, and on boiling with sodium carbonate yields

furylacetone, $\begin{array}{c} \text{CH} - \text{O} \\ | \quad \diagup \\ \text{CH} - \text{CH} \end{array} \geq \text{C} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$; this is a colourless liquid with an odour of horse-radish, and boils at 179—180°; its *semicarbazone* melts at 173—174° and its *oxime* boils at 135—140° under 25 mm. pressure.

M. A. W.

Dialkylmalonic Acids. HANS MEYER (*Ber.*, 1906, 39, 198—200. Compare E. Fischer and Dilthey, *Abstr.*, 1902, i, 269).—The dimethyl ester of dimethylmalonic acid is transformed into the amide,



when kept at the ordinary temperature with concentrated ammonia for

twenty-four hours and occasionally shaken. The corresponding diethyl ester is not transformed under similar conditions even after several weeks.

Dimethyl methylethylmalonate, $\text{CMeEt}(\text{CO}_2\text{Me})_2$, is a colourless oil distilling at $189\text{--}191^\circ$ (uncorr.) and *dimethyl diethylmalonate* distils at $204\text{--}205^\circ$. Dimethyl methylethylmalonate reacts with ammonia yielding *methylethylmalonamide*, $\text{CMeEt}(\text{CO}\cdot\text{NH}_2)_2$, which forms glistening crystals melting at $182\text{--}183^\circ$, and *methyl methylethylmalonamate*, $\text{CO}_2\text{Me}\cdot\text{CMeEt}\cdot\text{CO}\cdot\text{NH}_2$, which sublimes in glistening needles melting at $106\text{--}108^\circ$. Dimethyl- and diethyl-malonyl chlorides readily react with concentrated ammonium hydroxide yielding the corresponding diamides, whereas methylethylmalonyl chloride yields methylethylacetamide (Scheuble and Loebl, Abstr., 1904, i, 466). Fischer and Dilthey's views regarding the formation of the amides from the esters are adversely criticised. J. J. S.

Action of Ammonia on Itaconic and Pyrocinchonic Anhydrides. LUCIANO ROSSI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1905, [iii], 11, 254—258. Compare Foà, Abstr., 1904, i, 230).—The action of alcoholic ammonia on pyrocinchonic anhydride at different temperatures always yields pyrocinchonimide, which, however, melts at 113° if obtained at low temperatures, or at 118° if at high temperatures.

The action of liquid ammonia on pyrocinchonic anhydride yields pyrocinchonimide at the ordinary temperature, whilst at higher temperatures ($70\text{--}100^\circ$) a yellowish-brown syrup is obtained.

These results demonstrate, firstly, the great resistance exerted by the double linking of pyrocinchonic anhydride against the introduction of an amino-group, and, secondly, the great stability of the anhydride.

In the cold or at $70\text{--}80^\circ$, itaconic anhydride gives with liquid ammonia a yellowish-brown acid syrup which contains nitrogen, dissolves Peligot's copper oxide giving a green solution, and is probably a mono-amide. In the reaction at 100° , the yellowish-brown syrup obtained probably contains a small amount of amino-acid.

T. H. P.

Action of Zinc on a Mixture of Ethyl Orthoformate and Ethyl Bromopropionate. Synthesis of *s*-Trimethylisobutanetricarboxylic Acid. S. SOKOLOWSKY (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 889—896).—Zinc acts on a mixture of ethyl orthoformate (1 mol.) and ethyl α -bromopropionate (3 mols.) according to the equations: (1) $\text{CHMeBr}\cdot\text{CO}_2\text{Et} + \text{Zn} = \text{BrZn}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$; (2) $3\text{BrZn}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et} + \text{CH}(\text{OEt})_3 = \text{CH}(\text{CHMe}\cdot\text{CO}_2\text{Et})_3 + 3\text{ZnBr}\cdot\text{OEt}$.

Triethyl s-trimethylisobutanetricarboxylate [γ -ethylpentane- $\beta\delta\alpha$ -tricarboxylate], $\text{C}_{16}\text{H}_{28}\text{O}_6$, thus obtained, is a colourless, mobile liquid boiling at $200\text{--}201^\circ$. On hydrolysis, it yields the *monoethyl ester*,



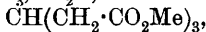
which crystallises from water in shining, white needles and from benzene in long, shining plates melting at 109° and is readily soluble in ether or chloroform. The *calcium*, $\text{Ca}(\text{C}_{12}\text{H}_{18}\text{O}_6)_2\cdot 4\text{H}_2\text{O}$, *barium*, and *sodium* salts of the monoethyl ester were prepared and analysed.

T. H. P.

Formation of Ethyl Sodiodicarboxyglutaconate from Ethyl Malonate, Sodium Ethoxide, and Chloroform. CARL COUTELLE (*J. pr. Chem.*, 1906, [ii], 73, 49—100. Compare Conrad and Guthzeit, *Abstr.*, 1883, 311).—Recrystallised ethyl sodiocarboxyglutaconate is obtained by Conrad and Guthzeit's reaction (*loc. cit.*), in a yield of 41·36 per cent. of the theoretical, if the absolute alcoholic solution of 4 mols. of sodium ethoxide is cooled to the laboratory temperature, 2 mols. of ethyl malonate and $1\frac{1}{4}$ mols. of chloroform added, and the mixture quickly boiled in a reflux apparatus. Smaller yields are obtained by varying the proportions of the reacting substances, or the temperature or order of mixing. Only 0·55 gram of the sodio-ester was obtained by the action of sodium and chloroform on 16 grams of ethyl malonate in benzene solution (compare Oppenheim and Precht, *this Journal*, 1876, ii, 69). The formation of ethyl sodiodicarboxyglutaconate is not due to the action of primarily formed ethyl *o*-formate on ethyl malonate, as when boiled with ethyl *o*-formate and sodium in alcoholic solution in a reflux apparatus, 32 grams of ethyl malonate yielded only 1·1 grams of the sodio-ester (compare Claisen, *Abstr.*, 1897, i, 592). The sodio-ester remains unchanged when boiled with chloroform in alcoholic solution.

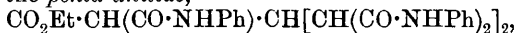
The formation of carbon monoxide, which must result from the decomposition of ethyl *o*-formate primarily formed, is shown by passing a current of hydrogen successively through the reacting mixture and a solution of cuprous chloride (Hullemann, *Abstr.*, 1890, 582). The salts which separate from the reaction mixture are sodium chloride, ethyl sodiomalonate, and sodium formate.

The reddish-brown residue obtained from the mother liquor, on distillation of the alcohol in a vacuum, was extracted successively with light petroleum, A, and with acetone, B. A. The light petroleum extract contains ethyl malonate and *ethyl isobutanehexacarboxylate*, $\text{CH}[\text{CH}(\text{CO}_2\text{Et})_2]_3$; this is a viscid, yellow oil, which boils at 235° under 13 mm. pressure, has an odour of onions, dissolves in alcoholic sodium ethoxide to form a dark red solution, decolorises immediately dilute potassium permanganate solution in presence of sodium carbonate, interacts with bromine in carbon disulphide, evolving hydrogen bromide, and when boiled with 10 per cent. hydrochloric acid is hydrolysed with formation of carbon dioxide and *isobutanetricarboxylic acid*. This is obtained as a brownish-red resin; it forms a *barium salt*, $\text{C}_{14}\text{H}_{14}\text{O}_{12}\text{Ba}_3\cdot 4\text{H}_2\text{O}$, and the *trimethyl ester*,



which is a colourless liquid boiling at 180—185° under 23 mm. pressure.

Hydrolysis of the ethyl hexacarboxylate with alcoholic potassium hydroxide leads to the formation of a red *oil*, which deposits needles melting at 129°, or with baryta water to the formation of barium formate and malonate (compare Bottomley and Perkin, *Trans.*, 1900, 77, 294; Guthzeit and Engelmann, *Abstr.*, 1902, i, 742). When heated with aniline at 150°, the ethyl hexacarboxylate forms malonanilide and the *penta-anilide*,



which crystallises from much alcohol and melts at 245°.

B. The acetone solution contains the last traces of ethyl sodiodicarboxyglutaconate, sodium malonate, and sodium formate. On treatment with sulphuric acid and ether, sodium formate yields an ethereal solution, which, when shaken with water and mercuric oxide, filtered, and heated in the water-bath, gives a grey precipitate of metallic mercury. When treated in the same way, sodium malonate forms a yellow precipitate, whilst glutaconic acid and ethyl sodiodicarboxyglutaconate do not form precipitates. In a mixture of formates and malonates, the formic acid is detected by this reaction, the malonic acid by the formation of its sparingly soluble barium salt.

On evaporation of the acetone solution, treatment of the residue with chloroform, and evaporation of the extract, a red, resinous *mass* is obtained; this contains probably a *sodio*-derivative of ethyl isobutanehexacarboxylate.

In the quantitative examination of the products of the reaction, the formic acid is estimated by Lieben's method (see Scala, *Abstr.*, 1891, 248), after precipitation of the malonic acid by means of barium chloride and alcohol, or after liberation of the formic acid by means of phosphoric acid and distillation in a current of steam, in which malonic acid is not volatile. As ethyl dicarboxyglutaconate is slightly volatile in a current of steam, the distillate is filtered after some hours, whereby a saturated solution of the ester is obtained; with mercuric chloride, 100 c.c. of this form 0.0551 gram of a precipitate, which weight is deducted from that of the mercuric chloride formed in the estimation of formic acid. As the barium derivative of ethyl dicarboxyglutaconate is only sparingly soluble in alcohol, it is precipitated partially together with the barium malonate; the amount of the latter which, when dried at 100°, has the composition $C_3H_2O_4Ba \cdot 5/6H_2O$ (compare Guthzeit and Bolam, *Abstr.*, 1898, i, 12) is determined by indirect analysis.

Ethyl sodiodicarboxyglutaconate and ethyl *o*-formate could not be estimated directly.

Under the conditions most favourable to the formation of ethyl sodiocarboxyglutaconate, 100 grams of ethyl malonate, 29 grams of sodium as sodium ethoxide, and 38 grams of chloroform interact to form 50.3 grams of ethyl sodiodicarboxyglutaconate, 32.6 grams of sodium malonate, 10.06 grams of ethyl sodioisobutanehexacarboxylate, 3.99 grams of the free ethyl hexacarboxylate, 3.27 grams of sodium formate, 0.18 gram of carbon monoxide, and 0.66 gram of ethyl *o*-formate, more than 13 grams of the ethyl malonate remaining unchanged.

G. Y.

Formaldehyde and Formate Formation. HANS EULER and ASTRID EULER (*Ber.*, 1906, 39, 36—39. Compare *Abstr.*, 1905, i, 633).—More exact measurements have given for the dissociation-constant of formaldehyde acting as a weak acid the value 1.4×10^{-14} at 0°, in close agreement with the approximate value 1×10^{-14} previously obtained with formaldehyde containing methyl alcohol. T. M. L.

Aldehydes as Acids. HANS EULER (*Ber.*, 1906, 39, 344—350. Compare Euler and Euler, *Abstr.*, 1905, i, 633).—Acetaldehyde has the dissociation constant $K = 0.8 \times 10^{-14}$ at 0°, as determined by the

depression of the freezing point of the solution of its sodium salt (Goldschmidt and Röder, Abstr., 1895, i, 657), or $K = 0.5 \times 10^{-14}$ at 1° , as determined by the conductivity of its sodium salt solution; the mean constant is $K = 0.7 \times 10^{-14}$ at 0° . As ammonia forms complex compounds, which are not electrolytically dissociated, and not salts, with acetaldehyde, the conductivity of aqueous ammonia is diminished on addition of the aldehyde.

Chloral hydrate has the dissociation constant $K = 1 \times 10^{-14}$ at 18° , as determined by the change in the conductivity of dilute ammonia which takes place on the addition of the aldehyde, or $K = 0.8 \times 10^{-14}$ at 18° , as calculated from the comparison of the conductivity of dilute solutions of its ammonium salt with the conductivities of similar solutions of the ammonium salts of boric acid and phenol.

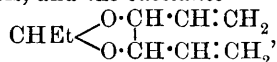
The salts of acetone with alkalis or with hydrogen chloride are dissociated hydrolytically to too great an extent to permit of the determination of the acid dissociation constant by either the conductivity or the cryoscopic method. Furfuraldehyde has only feeble salt-forming properties; its dissociation constant as an acid is $1/100$ of that of acetaldehyde.

The acid dissociation constant of dextrose, $K = 1.8 \times 10^{-13}$ at 0° , as determined with the sodium salt by the cryoscopic method, agrees with that calculated by Madsen (Abstr., 1901, ii, 228) from the rate of hydrolysis of the ester.

As in dextrose and laevulose solutions containing the equivalent amount of sodium hydroxide the hexose is present chiefly in the form of the ion, the rotation of an alkaline hexose solution is due principally to that of the sodium salt.

With sodium light at 0° , *N*-dextrose solution, when mixed with equal volumes of water, *N*-sodium hydroxide, *2N*-sodium hydroxide, *2N*-potassium hydroxide, and *N/2* sodium hydroxide has the rotations 10.4° , 8.1° , 7.8° , 7.8° , and 9.9° respectively, whilst *N/2* dextrose solution with equal volumes of water, *N/2* sodium hydroxide, and *2N*-sodium hydroxide, has the rotations 5.2° , 4.2° , and 4.2° respectively. G. Y.

The Reduction of Acraldehyde and some Derivatives of *s*-Divinyl Glycol ($\gamma\delta$ -Dihydroxy- $\alpha\epsilon$ -hexadiene). PIETER VAN ROMBURGH and W. VAN DORSEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 541—544. Compare Griner, Abstr., 1893, i, 237).—When reduced with zinc dust and glacial acetic acid, acraldehyde yields allyl and propyl alcohols, and the substance

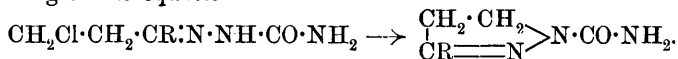


which is formed also by heating propaldehyde with *s*-divinyl glycol at 90° for six days. It is a neutral liquid, which boils at 59.5 — 60° under 15 mm. pressure, is not decomposed by potassium hydroxide, sodium, or phosphorus pentachloride, and does not form a benzoyl derivative when treated with benzoyl chloride and pyridine; it yields an odour of aldehyde, and forms a brownish-black, resinous mass when treated with dilute acids, and forms an *additive compound* with bromine in carbon tetrachloride solution.

The *diformate*, formed by heating *s*-divinyl glycol with formic acid,

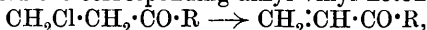
is a colourless liquid which boils at 109° under 20 mm. pressure and has the sp. gr. 1·0747 at 11°. G. Y.

β-Chloroethyl Ketones and Alkyl Vinyl Ketones. EDMOND E. BLAISE and M. MAIRE (*Compt. rend.*, 1906, [142, 215—217].—β-Chloroethyl alkyl ketones of the type $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{R}$, readily obtained by the action of β-chloropropionyl chloride on the corresponding zinc alkyl, are liquids with a faint odour; their semicarbazones are unstable and readily converted into the carbamide of a pyrazole according to the equation



Ethyl β-chloroethyl ketone boils at 68° under 20 mm. pressure.
β-Chloroethyl propyl ketone boils at 73° under 10 mm. pressure.
β-Chloroethyl isobutyl ketone boils at 80° under 12 mm. pressure.

When the alkyl β-chloroethyl ketones are boiled with diethyl-aniline, they yield the corresponding alkyl vinyl ketones,



in the form of mobile liquids with an intensely penetrating odour; *ethyl vinyl ketone* boils at 31° under 47 mm. pressure; *propyl vinyl ketone* boils at 24° under 10 mm. pressure; and *isobutyl vinyl ketone* boils at 32° under 10 mm. pressure. These compounds polymerise rapidly under the action of heat or of alkalis, and yield semicarbazosemicarbazones with semicarbazide, hydroxylamino-oximes with hydroxylamine, pyrazoles with hydrazine, or phenylpyrazoles with phenylhydrazine; the last compounds give an intense violet-red colour with a trace of nitric acid. The pyrazoles are basic liquids forming salts, platinichlorides, picrates, and phenylcarbamides, and with secondary bases yielding additive compounds of the type $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{R}$, which are also basic and form picrates and platinichlorides. *Ethyl β-diethylaminoethyl ketone* boils at 80° under 10 mm. pressure, and *ethyl β-piperidinoethyl ketone* boils at 107° under 11 mm. pressure. M. A. W.

Formation of Sugar from Formaldehyde. HANS EULER and ASTRID EULER (*Ber.*, 1906, 39, 39—45).—The action of alkalis on formaldehyde leads both to the formation of formates and the formation of sugars, but the latter process is not directly dependent on, and does not run parallel with, the former; addition of formate does not affect the rate at which sugar is formed. Curves are given to show the rate at which sodium carbonate is neutralised by formaldehyde previously to the formation of sugar. The concentration of formaldehyde at which sugar-formation sets in is dependent on the initial concentrations of the sodium carbonate and of the aldehyde, and sugar-formation never appears to occur until a part of the aldehyde has been converted into formate and alcohol; the most suitable concentration is nearly half an equivalent of soda for each equivalent of aldehyde. Experiments were also made with calcium carbonate as a condensing agent, the increased time required being compensated for by the increased stability of the sugar and the more constant composition of the solutions; it was noticed that sugar formation proceeds very

slowly at first, but after boiling for several hours, proceeds very rapidly to a limit; this is explained by the formation of intermediate compounds, and the presence of glycollaldehyde was actually proved.

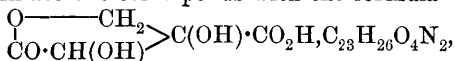
T. M. L.

Formation of *i*-Arabinoketose from Formaldehyde. HANS EULER and ASTRID EULER (*Ber.*, 1906, 39, 45—51).—When formaldehyde is condensed by means of calcium carbonate, the chief product is a pentose, which was identified by means of its osazone and phenylmethyl-osazone, and by oxidation with bromine and with nitric acid as *i*-arabinoketose. A small amount of a hexose is also produced. If the action of the alkali is stopped before half the formaldehyde has disappeared, glycollaldehyde is one of the chief products, but glyceraldehyde could not be detected.

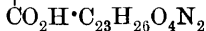
T. M. L.

Apiose. EDUARD VONGERICHTEN and FR. MÜLLER (*Ber.*, 1906, 39, 235—240. Compare *Abstr.*, 1901, i, 40, 646; 1902, i, 425).—Apiose obtained from the leaves of parsley is identical with that obtained from the seeds. *Apiose phenylbenzylhydrazone*, $C_{18}H_{22}O_4N_2$, separates from benzene solution in colourless, crystalline flocks which melt at 135° . By the action of formaldehyde, apiose is recovered as a colourless syrup, which in aqueous solution has $[\alpha]_D + 3.8^\circ$ at 20° , and is in all respects identical with the apiose from which the hydrazone was prepared.

At 50° , the oxidation of calcium apionate by three times its weight of nitric acid of sp. gr. 1.2 results in the formation of an acid, isomeric with trihydroxyglutaric acid, the calcium salt of which has $[\alpha]_D + 6.58^\circ$ at 20° . The oxidation of the acid by silver oxide produces glycollic acid. Neutralised with brucine, the acid yields two salts; the one insoluble in acetone corresponds with the formula



has $[\alpha]_D - 23.7^\circ$ at 20° , and the lactonic acid obtained from it is converted on boiling with baryta water into the dibasic hydroxy-acid. The other *brucine* salt is soluble in acetone, melts at $148\text{--}150^\circ$, and has $[\alpha]_D - 27.2^\circ$ at 20° ; the analytical data agree with the formula $\text{CH}_2(\text{OH}) \cdot \text{C}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}, C_{23}H_{26}O_4N_2$.



Of the known trihydroxyglutaric acids, only the inactive ribotrihydroxyglutaric acid is capable of lactone-formation; it is quite different from the hydroxymethyltartaric acid described above.

C. S.

Action of Oxygen on Aliphatic Amines in Presence of Copper. WILHELM TRAUBE and ALBERT SCHÖNEWALD (*Ber.*, 1906, 39, 178—184).—When an aqueous solution of ethylamine is shaken for several days with copper powder in the presence of oxygen at the ordinary temperature, a copious absorption of oxygen is observed (some 7 litres for 10 grams of ethylamine), the copper is oxidised to the hydroxide, and the ethylamine to acetaldehyde and ammonia. Nitrogen and nitrous acid do not appear to be formed.

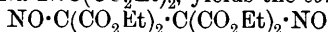
When a 5 per cent. solution of aldehyde-ammonia is shaken with copper and oxygen, very little oxidation occurs. It is thus possible that the primary oxidation product in the earlier experiments was aldehyde-ammonia and not free aldehyde and free ammonia, since the latter would tend to become oxidised to nitrous acid.

Methylamine reacts in much the same manner as ethylamine, yielding formaldehyde and ammonia.

Sodium-glycine, copper, and oxygen yield considerable quantities of nitrous acid and probably glyoxylic acid. J. J. S.

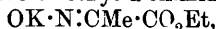
Electro-synthesis in the Oximo-ether Group. CELSO ULPANI and G. A. RODANO (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 601—607. Compare Abstr., 1905, i, 260).—Using platinum electrodes and a current intensity of 0.2—0.25 ampere, the authors have electrolysed the sodium or potassium derivative of ethyl oximinomalonate, ethyl α -oximinopropionate, and ethyl α -oximinobutyrate. These compounds, which have the general formula $\text{CRR}'\text{NONa}$, are decomposed into metal, which evolves hydrogen at the negative pole, and the anion $\text{CRR}'\text{NO}^-$; of the last, two groups combine at the positive pole.

In this way, the sodium hydrogen derivative of ethyl oximinomalonate, $\text{OH}\cdot\text{N}:\text{C}(\text{CO}_2\text{Et})_2, \text{ONa}\cdot\text{N}:\text{C}(\text{CO}_2\text{Et})_2$, yields the compound



as an oil which is insoluble in alkali and yields Liebermann's reaction characteristic of true nitroso-compounds.

The potassium derivative of ethyl α -oximinopropionate,



yields the compound $\text{NO}\cdot\text{CMe}(\text{CO}_2\text{Et})\cdot\text{CMe}(\text{CO}_2\text{Et})\cdot\text{NO}$ as an oil, which is insoluble in alkali and gives Liebermann's reaction.

The potassium derivative of ethyl α -oximinobutyrate yields the compound $\text{CH}_2\text{Me}\cdot\text{C}(\text{NO})(\text{CO}_2\text{Et})\cdot\text{C}(\text{NO})(\text{CO}_2\text{Et})\cdot\text{CH}_2\text{Me}$, which is an oil; it is soluble in alkali and giving Liebermann's reaction. T. H. P.

Isolation of Amino-acids. MAX SIEGFRIED (*Ber.*, 1906, 39, 397—401. Compare Abstr., 1905, i, 59; ii, 332).—Glycine is readily precipitated as *barium carbaminoacetate*, $\begin{matrix} \text{CH}_2\cdot\text{CO}_2 \\ \text{NH}_2\cdot\text{CO}_2 \end{matrix} > \text{Ba}$, when carbon dioxide is led into a solution of the amino-acid in baryta water at 0° until phenolphthalein is decolorised and the mixture then kept for some time at 0°. Better yields are obtained when more baryta water is added after the carbon dioxide has been led in, and when the precipitate is washed with dilute barium hydroxide solution instead of with water.

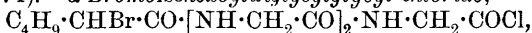
Pure glycine is obtained when the barium salt is decomposed with ammonium carbonate solution, filtered, and the solution evaporated.

Glycylglycine yields a similar *barium* salt, $\text{C}_5\text{H}_6\text{O}_5\text{N}_2\text{Ba}$, which is much more readily soluble in water. It is most readily obtained by the addition of alcohol, and when decomposed with ammonium carbonate yields pure glycylglycine.

Lysine and albumoses give similar barium salts. Glyeine and

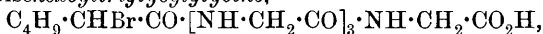
alanine can be separated with great readiness by this method, as the barium salt from alanine is readily soluble in water. J. J. S.

Synthesis of Polypeptides. XIV. EMIL FISCHER (*Ber.*, 1905, 39, 453—474).— *α -Bromoisohexoyldiglycylglycyl chloride*,



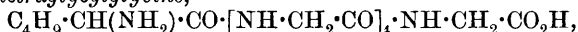
prepared by the action of acetyl chloride and phosphorus pentachloride on bromoisohexoyldiglycylglycine, freshly crystallised from alcohol, is obtained as a colourless powder easily decomposed by water. It reacts with glycine ethyl ester in chloroform solution to form *α -bromoisohexoyltriglycylglycine ethyl ester*, crystallising in colourless, microscopic needles which become brown at 235° (corr.) and melt and evolve gas at 241° (corr.).

α -Bromoisohexoyltriglycylglycine,



prepared by the interaction of the above chloride with glycine, crystallises in microscopic, colourless plates, which become brown at 212° (corr.) and melt and decompose at 218° (corr.). *α -Bromoisohexoyltetraglycylglycine*, $\text{C}_4\text{H}_9\cdot\text{CHBr}\cdot\text{CO}\cdot[\text{NH}\cdot\text{CH}_2\cdot\text{CO}]_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, formed by the interaction of the chloride with glycine anhydride, is obtained as a crystalline powder which turns brown at 230° (corr.) and melts at 237° (corr.).

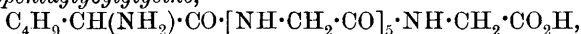
Leucyltetraglycylglycine,



prepared by the action of aqueous ammonia on the foregoing, forms a colourless, crystalline powder which on heating becomes coloured at 225° (corr.) and partially melts and decomposes at 240° (corr.). It shows a marked biuret coloration.

α -Bromoisohexoylpentaglycylglycine, formed by the interaction of diglycylglycine with bromoisohexoyldiglycylglycine chloride, crystallises in colourless aggregates of no definite crystalline form, which become coloured at 220° (corr.) and melt at 250° (corr.).

Leucylpentaglycylglycine,



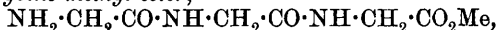
prepared by the action of aqueous ammonia on the foregoing, also has no definite crystalline structure, becomes yellow at 220° , and decomposes at 270° . It gives a strong biuret coloration.

A method for the preparation of *d*-alanine from silk is described at length. This crystallises from water in well-formed, centimetre long, rhombic crystals [$a:b:c=0.9784:1:0.4924$]. *d*- and *l*-Alanine have the same taste. The hydrochloride has $[\alpha]_D +10.3^\circ$ at 20° ; the racemate can only be removed from the active substance by crystallisation of the free amino-acid. *d-Alanyl-d-alanine* crystallises in centimetre long, thin prisms, has $[\alpha]_D -21.6^\circ$ at 20° , and melts and decomposes at about 298° (corr.), some 20° higher than the racemic alanylalanine. In hydrochloric acid solution, it has $[\alpha]_D$ about -36.5° at 20° ; on heating with 10 per cent. acid, it is converted into alanine, about 73 per cent. being changed after five hours and 87 per cent. after seven and a half hours' heating.

d-Alanine anhydride (*cis-dimethyldiketopiperazine*) crystallises in

silvery, glistening leaflets which melt at 297° (corr.) and have $[\alpha]_D - 28.8^{\circ}$ at 20° ; the inactive compound melts at 282° .

Diglycylglycine methyl ester,



prepared by the action of methyl alcohol and hydrogen chloride on the tripeptide, crystallises in long needles grouped in stellar aggregates which melt indefinitely about 111° (corr.); the *hydrochloride* crystallises in glistening, small plates, sinters at 200° , and melts and decomposes at 204° (corr.).

Pentaglycylglycine methyl ester,



prepared by heating the powdered diglycylglycine methyl ester at 100° , when it condenses with elimination of methyl alcohol, when separated from hot water forms a fine precipitate having no definite crystalline form and decomposing between 200° and 300° .

Pentaglycylglycine, prepared by the action of sodium hydroxide on the foregoing, is obtained as a colourless powder very sparingly soluble in water, which begins to decompose above 256° (corr.) and gives the biuret coloration; the *nitrate* crystallises in microscopic needles melting and decomposing at about 240° (corr.).

Along with the above, what is probably a still higher condensation product is obtained on heating diglycylglycine methyl ester: this gives a strong biuret reaction.

E. F. A.

Amino- and Diazo-malonic Esters. OSCAR PILOTY and J. NERESHEIMER (*Ber.*, 1906, 39, 514—517).—*Ethyl aminomalonate hydrochloride*, $\text{NH}_2 \cdot \text{CH}(\text{CO}_2\text{Et})_2 \cdot \text{HCl}$, is obtained by passing dry hydrogen chloride into absolute alcohol containing sodium aminomalonate in suspension, or by reducing ethyl isonitrosomalonate with aluminium amalgam. It crystallises from acetone in small, colourless needles and melts and decomposes at 162° . The *hydrochloride* of the corresponding *methyl ester* is easily soluble in water, and is precipitated from methyl-alcoholic solution by the addition of ether in small, colourless, rhombic crystals, frequently twinned, which melt and decompose at 159° . Each of the preceding ester hydrochlorides on treatment with ammonia yields aminomalonamide, the melting point of which is 192° , 10° higher than the value found by Conrad and Guthzeit (*Abstr.*, 1882, 947). When a cold concentrated aqueous solution of ethyl aminomalonate hydrochloride is treated with nitrous acid and the product extracted with ether, an intensely yellow ethereal solution is obtained; after evaporation of the ether, a viscous, yellow oil remains, which is probably *ethyl diazomalonate*, since it has an odour resembling that of ethyl diazoacetate, explodes on heating, and is decomposed by mineral acids with violent evolution of nitrogen.

C. S.

Cyanuric Acid as a Pseudo-acid. ARTHUR HANTZSCH (*Ber.*, 1906, 39, 139—153. Compare Ponomareff, *Abstr.*, 1886, 216).—Cyanuric acid is a tricarbimide, and as a complete pseudo-acid should be termed pseudocyanuric acid. The three pseudo-groups $\text{CO} \cdot \text{NH}$ can be transformed into the groups $\text{C}(\text{OH}) \cdot \text{N}$, which can then form

salts. The transformation proceeds in three distinct stages; the first stage proceeds most readily and the last least readily. The first group is partially transformed by water alone, as the aqueous solution of cyanuric acid behaves as a feeble monobasic acid (at 25° , $K = 0.000018$). Preparations of the acid from different sources all give the same result. The temperature-coefficient of the conductivity increases rapidly with the temperature, as is also the case with other pseudo-acids. The transformation of the first $\text{CO}\cdot\text{NH}$ group is complete in the presence of one equivalent of alkali, as the primary metallic cyanurates, $\text{C}_3\text{N}_3\text{O}_3\text{H}_2\text{X}$, are neutral to phenolphthalein. Thus, when titrated with $N/10$ sodium hydroxide in the presence of phenolphthalein, cyanuric acid acts as a monobasic acid.

These primary cyanurates have the same properties, whether prepared from concentrated or dilute, from hot or cold solutions. The following are described: *Ammonium* salt, $\text{C}_3\text{N}_3\text{O}_3\text{H}_2\text{NH}_4\cdot\text{H}_2\text{O}$; this readily loses ammonia on exposure to the air, and at 130° leaves a residue of pure cyanuric acid. *Calcium* salt, $(\text{C}_3\text{N}_3\text{O}_3\text{H}_2)_2\text{Ca}\cdot 8\text{H}_2\text{O}$, slender needles only sparingly soluble in hot water; it retains part of its water even at 200° . *Magnesium* salt, $(\text{C}_3\text{N}_3\text{O}_3\text{H}_2)_2\text{Mg}\cdot 14\text{H}_2\text{O}$, needles readily soluble in hot water; when heated it decomposes before it is completely dehydrated. The same salt is obtained when the secondary sodium salt is treated with magnesia mixture.

The second $\text{CO}\cdot\text{NH}$ group is only partially transformed into $\text{C}(\text{OX})\cdot\text{N}$ when treated with two equivalents of alkali in aqueous solution; solutions of the composition $\text{C}_3\text{N}_3\text{O}_3\text{H}_3\cdot 2\text{NaOH}$ are strongly hydrolysed. The transformation is, however, complete at the ordinary temperature when the secondary salt is insoluble, for example, calcium, barium, and silver salts. The following secondary salts are described: *Sodium* salt, $\text{C}_3\text{N}_3\text{O}_3\text{HNa}_2\cdot\text{H}_2\text{O}$, which is precipitated even when a large excess of alkali is present. It crystallises in needles and may be dehydrated at 130° ; its aqueous solution is strongly alkaline and hydrolysed to an appreciable extent, even more strongly than disodium hydrogen phosphate, as is shown by conductivity determinations. *Calcium* salt, $\text{C}_3\text{N}_3\text{O}_3\text{HCa}\cdot 3\text{H}_2\text{O}$, is precipitated at 0° or at the ordinary temperature, and may be dehydrated at 165° . At 100° , it becomes converted into the monohydrate, $\text{C}_3\text{N}_3\text{O}_3\text{HCa}\cdot\text{H}_2\text{O}$, which is also formed when the salt is precipitated from boiling solutions or from the trisodium salt at 0° . It also may be dehydrated at 165° . The conversion of the monohydrate into the trihydrate has not been accomplished. *Barium* salts, $\text{C}_3\text{N}_3\text{O}_3\text{HBa}\cdot 3\text{H}_2\text{O}$ and $\text{C}_3\text{N}_3\text{O}_3\text{HBa}\cdot\text{H}_2\text{O}$. The trihydrate cannot be transformed into the monohydrate by heating in a thermostat. *Silver* salt, $\text{C}_3\text{N}_3\text{O}_3\text{HAg}_2\cdot\text{H}_2\text{O}$, is precipitated from both the mono- and di-sodium salts. The anhydrous salt may be obtained by heating the monohydrate or by precipitating the salt at 100° .

The third $\text{CO}\cdot\text{NH}$ group is not transformed at the ordinary temperature when a large excess of alkali is present, even when the tertiary salts are insoluble. At the ordinary temperature, cyanuric acid is a dibasic acid only. The secondary salts are all pseudo-acids, either $\text{N} \begin{smallmatrix} \text{CO} - \text{NH} \\ \diagup \quad \diagdown \end{smallmatrix} \text{C} \cdot \text{OX}$ or $\text{NH} \begin{smallmatrix} \text{C}(\text{OX}) \cdot \text{N} \\ \diagdown \quad \diagup \end{smallmatrix} \text{CO}$. The third $\text{CO}\cdot\text{NH}$ group is transformed at 100° , and tertiary salts can then be obtained.

The tertiary sodium salt, $C_3N_3O_3Na_3 \cdot H_2O$, is precipitated in slender needles when a cold solution of the acid in excess of 20 per cent. sodium hydroxide is heated to 100° . It cannot be recrystallised on account of the readiness with which it is hydrolysed and decomposed by carbon dioxide; it appears to be stable in presence of its mother liquor. It may also be precipitated by the addition of alcohol to a solution of the acid in sodium hydroxide (three equivalents). Two equivalents of alkali in its solution may be titrated by standard acid, using phenolphthalein as indicator. The conductivity of its aqueous solution has a high value due to considerable hydrolysis, and in this respect is identical with the solution of the acid in sodium hydroxide (three equivalents). The tertiary *calcium*, *barium*, and *silver* salts are all anhydrous, and are only precipitated at 100° ; at the ordinary temperature, secondary salts are usually obtained. In the preparation of the tertiary salts, pure sodium hydroxide must be employed, and the solutions must be protected from atmospheric carbon dioxide.

When the silver salt is treated with sodium hydroxide solution, the secondary silver salt and silver oxide are formed.

The tertiary *mercuric* salt may be obtained at 0° or at the ordinary temperature.

When cyanuric acid is evaporated with mercuric chloride solution, the double compound, $2C_3N_3O_3H_3 \cdot HgCl_2 \cdot 4H_2O$, is obtained in the form of lustrous plates which effloresce on exposure to the air.

Aluminium salts could not be prepared.

J. J. S.

Acetylenic Amides and Nitriles. CHARLES MOUREU and I. LAZENNEC (*Compt. rend.*, 1906, 142, 211—214).—Acetylenic amides of the type $R \cdot C \equiv C \cdot CO \cdot NH_2$ are readily prepared by the action of ammonia on the corresponding ester. Amylpropiolamide,

$CH_3 \cdot [CH_2]_4 \cdot C \equiv C \cdot CO \cdot NH_2$
(compare Abstr., 1903, i, 312), melts at 91° ; *hexylpropiolamide*, $CH_3 \cdot [CH_2]_5 \cdot C \equiv C \cdot CO \cdot NH_2$, melts at 92° , and *phenylpropiolamide* melts at 106° (compare Stockhauser and Gattermann, Abstr., 1893, i, 163); they crystallise in colourless plates, are readily soluble in alcohol, methyl alcohol, or chloroform, less soluble in ether, and sparingly so in water; phenylpropiolamide is converted into benzoylacetamide by the action of sulphuric acid and water (compare Obrégia, Abstr., 1892, 324).

The acetylenic nitriles $R \cdot C \equiv C \cdot CN$ are obtained by the action of phosphoric oxide on the corresponding amide. *Amylpropiolonitrile*, $CH_3 \cdot [CH_2]_4 \cdot C \equiv C \cdot CN$, boils at 194 — 196° (corr.) under 760 mm. or 80 — 81° under 13 mm. pressure, has a sp. gr. 0.8508 at $13^\circ/4^\circ$, and n_D 1.4553 at 13° ; *hexylpropiolonitrile*, $CH_3 \cdot [CH_2]_5 \cdot C \equiv C \cdot CN$, boils at 212 — 213° (corr.) under normal, or 95 — 96° under 13 mm. pressure, has a sp. gr. 0.8493 at $14.4^\circ/4^\circ$ and n_D 1.45637 at 14.4° ; *phenylpropiolonitrile*, $CPh \cdot C \cdot CN$, melts at 41° , boils at 228 — 229° (corr.) under normal, or at 105 — 106° under 13 mm. pressure, has a sp. gr. 1.0046 at $41.5^\circ/4^\circ$, and n_D 1.58535 at 41.5° (compare *Bull. Soc. chim.*, 1902, [iii], 26, 99; Claisen, Abstr., 1904, i, 14). By the action of alcoholic potassium hydroxide, the acetylenic nitriles yield the corresponding acid and compounds of the type $R \cdot C(OEt) \cdot CH \cdot CN$,

and by the action of sulphuric acid the nitriles of the aliphatic series yield the corresponding acid, whilst phenylpropionitrile yields benzoylacetamide.

M. A. W.

Action of Potassium Cyanide on Sodium Tetrathionate and Dithionate. AUGUST GUTMANN (*Ber.*, 1906, 39, 509—513).—The reaction between sodium tetrathionate and potassium cyanide in the presence of alkali was quantitatively examined and shown to follow a course represented by the equation: $\text{Na}_2\text{S}_4\text{O}_6 + 2\text{CNK} + 2\text{NaOH} = 2\text{CNSK} + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}$. Potassium cyanate and potassium sulphite do not react either at the ordinary temperature or on warming. Sodium dithionate is stable towards potassium cyanide even at 100°.

C. S.

Detection and Precipitation of the Ferrous Iron in Aqueous Solutions of Potassium Ferrocyanide. FRITZ HABER (*Zeit. Elektrochem.*, 1905, 11, 846—849).—Berthelot (*Abstr.*, 1901, i, 20) showed that alkali sulphides produce a precipitate of ferrous sulphide in solutions of potassium ferrocyanide. The author finds that this only occurs in the light. Air passed through a solution of potassium ferrocyanide exposed to light precipitates ferric hydroxide.

T. E.

Potassium Mercuric Ferrocyanide. GUSTAVE FERNEKES (*J. Amer. Chem. Soc.*, 1906, 28, 87—90).—A detailed account is given of the preparation of *potassium mercuric ferrocyanide*, $\text{K}_2\text{HgFe}(\text{CN})_6$, by the interaction of mercuric chloride and potassium ferrocyanide. The salt is obtained as a fine, faintly blue powder, is insoluble in water, and is decomposed by hydrochloric acid with formation of Prussian blue, mercuric chloride, and hydroferrocyanic acid; when treated with sodium hydroxide, ferric hydroxide, mercuric oxide, and potassium ferrocyanide are produced.

E. G.

Compounds of Hydroferrocyanic, Hydroferricyanic, and Hydrocobalticyanic Acids, with Furfuraldehyde and with Nitrogen Derivatives. FRIEDRICH WAGENER and BERNHARD TOLLENS (*Ber.*, 1906, 39, 410—423. Compare Baeyer and Villiger, *Abstr.*, 1901, i, 658; 1902, i, 112, 355).—Furan and furfuraldehyde yield unstable additive compounds with hydroferrocyanic and hydroferricyanic acids. The composition of the compounds has not been settled, as they readily lose the basic constituent and yield the pure acid.

Trimethylamine cobalticyanide, $2\text{NMe}_3 \cdot \text{H}_3\text{CoC}_6\text{N}_6 \cdot \text{H}_2\text{O}$, forms a thick, white, crystalline precipitate readily soluble in water, but is thrown down by alcohol; the *ferricyanide* forms small, yellow crystals and begins to decompose at 175°; the *ferrocyanide* crystallises in pale yellow, octahedral crystals and begins to decompose at 140°. Tetramethylammonium hydroxide and hydrocobalticyanic acid yield the compound $2\text{NMe}_4 \cdot \text{OH} \cdot \text{H}_3\text{CoC}_6\text{N}_6$, which crystallises from hot water in colourless plates. It begins to decompose at 203°. The corresponding *ferricyanide* forms orange-yellow plates and begins to decompose at about 175°. The *ferrocyanide* forms small, pale yellow crystals.

Hexamethylenetetramine cobalticyanide, $2\text{C}_6\text{H}_{12}\text{N}_4 \cdot \text{H}_3\text{CoC}_6\text{N}_6 \cdot 3\frac{1}{2}\text{H}_2\text{O}$, forms colourless crystals and decomposes at about 160° ; *hexamethylenetetramine ferricyanide*, $2\text{C}_6\text{H}_{12}\text{N}_4 \cdot \text{H}_3\text{FeC}_6\text{N}_6 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, is a reddish-brown precipitate, and the *ferrocyanide*,
 $2\text{C}_6\text{H}_{12}\text{N}_4 \cdot \text{H}_4\text{FeC}_6\text{N}_6 \cdot 7\frac{1}{2}\text{H}_2\text{O}$,

is greenish-white.

Pyridine cobalticyanide, $2\text{C}_5\text{NH}_5 \cdot \text{H}_3\text{CoC}_6\text{N}_6 \cdot 2\text{H}_2\text{O}$, forms white prisms and decomposes at 175° , the corresponding *ferricyanide* forms yellowish-brown prisms and decomposes at 125° , and the *ferrocyanide* forms yellow prisms decomposing at 135° . *Piperidine cobalticyanide*, $2\text{C}_5\text{NH}_{11} \cdot \text{H}_3\text{CoC}_6\text{N}_6 \cdot 2\text{H}_2\text{O}$, crystallises in colourless needles and decomposes at 160° ; the *ferricyanide* forms monohydrated, yellow crystals decomposing at 125° , and the *ferrocyanide* (with $1\frac{1}{2}\text{H}_2\text{O}$), colourless, octahedral crystals decomposing at 125° . *Quinoline cobalticyanide*, $3\text{C}_9\text{NH}_7 \cdot \text{H}_3\text{CoC}_6\text{N}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$, forms colourless crystals decomposing at 190° ; the *ferricyanide* (with H_2O), sulphur-yellow crystals, decomposing at 155° , and the *ferrocyanide*, $2\text{C}_9\text{NH}_7 \cdot \text{H}_4\text{FeC}_6\text{N}_6$, yellowish-brown plates.

Betaine cobalticyanide, $2\text{C}_5\text{H}_{11}\text{O}_2\text{N} \cdot \text{H}_3\text{CoC}_6\text{N}_6 \cdot 2\text{H}_2\text{O}$, forms long, colourless needles, decomposing at 130° ; the *ferricyanide* (with $4\text{H}_2\text{O}$), yellow needles, decomposing at 130° , and the *ferrocyanide* (with $4\text{H}_2\text{O}$), greenish-white needles decomposing at 140° .

Phenylhydrazine ferrocyanide, $4\text{C}_6\text{H}_8\text{N}_2 \cdot \text{H}_4\text{FeC}_6\text{N}_6$, forms colourless, minute plates. J. J. S.

Secondary Arsines. WILLIAM M. DEHN and BURTON B. WILCOX (*Amer. Chem. J.*, 1906, **35**, 1—54).—A method is described for preparing dimethylarsine by the reduction of cacodyl oxide. Dimethylarsine boils at 35.6° under 747 mm. and at 55° under 1.74 atmospheres pressure, and has a sp. gr. 1.213 at 29° .

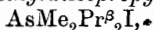
When dimethylarsine is heated in a sealed tube for an hour at 335° in presence of not more than traces of air, the inner surface of the tube becomes coated with a lustrous, black substance which appears to be the black polymeride of methylarsine described by Auger (*Abstr.*, 1904, i, 724); a gas which is either methane or a mixture of ethane and hydrogen is produced simultaneously.

On allowing dimethylarsine to oxidise slowly in the air, the erytharsine, $(\text{AsCH}_3)_4 \cdot \text{As}_2\text{O}_3$, described by Bunsen (*Annalen*, 1842, **42**, 41) is formed. When the arsine is treated with pure oxygen, ethane is produced together with a black solid which consists of a mixture of the polymeride of methylarsine and metallic arsenic. The oxidation is always accompanied by the formation of cacodyl oxide and cacodylic acid.

By the action of bromine on dimethylarsine, hydrogen bromide, hydrogen, and cacodyl bromide are produced together with *bromocacodyl hydrobromide*, $\text{AsMe}_2\text{Br} \cdot \text{HBr}$, which forms white, tabular crystals, is soluble in hot chloroform, insoluble in ether, and is decomposed by water into cacodyl bromide and hydrogen bromide. Chlorine reacts with the arsine with formation of methylarsine dichloride. When dimethylarsine is treated with iodine in a sealed tube, *iodocacodyl hydriodide*, $\text{AsMe}_2\text{I} \cdot \text{HI}$, is obtained, which crystallises in large,

pale yellow needles, softens and darkens at 160° , melts at 175° , is soluble in alcohol, and is easily decomposed by water. By the action of aqueous iodine on the arsine, cacodylic acid and hydrogen iodide are produced.

Dimethyldiisobutylarsonium iodide, $\text{AsMe}_2(\text{C}_4\text{H}_9)_2\text{I}$, obtained by heating dimethylarsine with isobutyl iodide in a sealed tube at 110° for five hours, is a white, crystalline substance which melts at 155° and is soluble in alcohol or chloroform, but insoluble in ether. *Dimethyldicetylarsonium iodide*, $\text{AsMe}_2(\text{C}_{16}\text{H}_{33})_2\text{I}$, forms white crystals and melts at $53-54^{\circ}$. *Dimethyldiisopropylarsonium iodide*,



is a white, crystalline solid which does not melt below 230° . *Dimethyldiallylarsonium iodide* forms light yellow crystals. *Dimethylallylarsine*, $\text{AsMe}_2\cdot\text{C}_3\text{H}_5$, obtained by the action of allyl iodide (1 mol.) on dimethylarsine (1 mol.), is a pale yellow liquid which boils at about 160° , is irritating to the eyes and skin, and has a strong, disagreeable odour; when heated with methyl iodide, it is converted into trimethylallylarsonium iodide. Dimethylallylarsine reacts violently with bromine in ethereal solution with formation of the *dibromide*, $\text{C}_3\text{H}_5\cdot\text{AsMe}_2\text{Br}_2$, as a yellow, flocculent precipitate.

The secondary arsines possess basic properties. When dimethylarsine is treated with dry hydrogen bromide at -10° , a hydrobromide seems to be formed which readily undergoes decomposition at the ordinary temperature with formation of cacodyl bromide and hydrogen. Dry hydrogen iodide unites with dimethylarsine to form a white, crystalline compound which decomposes into cacodyl iodide and hydrogen. By the action of concentrated sulphuric acid on the arsine, the *sulphate*, $2\text{AsHMe}_2\cdot\text{H}_2\text{SO}_4$, is produced, together with cacodyl sulphide and cacodylic acid.

Nitrous oxide has no action on dimethylarsine, but nitric oxide, nitric peroxide, nitrous acid, and nitric acid react with the base with formation of nitrous oxide or nitrogen, the arsine being converted into various oxidation products, of which cacodylic acid is the most abundant. Chromic acid rapidly oxidises the arsine to dicacodyl or cacodylic acid. An aqueous solution of potassium dichromate is instantly reduced by the arsine. When dimethylarsine is treated with molybdic acid in presence of water, molybdenum dioxide and cacodylic acid are slowly formed. Lead peroxide reacts with the arsine with formation of dicacodyl, lead cacodylate, and lead. Ferric chloride is immediately reduced by the arsine with production of ferrous chloride and cacodyl chloride. If molecular quantities of dimethylarsine and cacodyl chloride are heated together in a sealed tube for two or three hours at 100° , dicacodyl and hydrogen chloride are produced. A study was made of the action of platonic chloride on dimethylarsine, but no definite conclusions could be drawn as to the composition of the products obtained. The compound obtained by Bunsen (*Jahrb. Chem.*, 21, 500) by the action of platonic chloride on cacodyl chloride, to which he assigned the formula $\text{AsMe}_2\text{Cl}\cdot\text{PtO}\cdot\text{H}_2\text{O}$, is unstable and varies in composition according to the method of preparation. Auric chloride reacts with dimethylarsine with formation of dicacodyl, cacodyl chloride, cacodylic acid, and a precipitate of indefinite com-

position. Dimethylarsine rapidly reduces silver nitrate and mercuric chloride to the metal. By the action of potassium ferricyanide on the arsine, potassium ferrocyanide, dicacodyl, and potassium cacodylate are produced. Sulphur reacts readily with the arsine with formation of cacodyl sulphide or disulphide according to the quantity of sulphur used. By the action of liquid sulphur dioxide on the arsine, cacodyl disulphide, methylarsine sulphide, trimethylarsine sulphide, and cacodylic acid are formed. When dimethylarsine is treated with sulphur dichloride, cacodyl chloride, sulphur, and hydrogen sulphide are produced. Stannic chloride reacts with the arsine with formation of hydrogen chloride and the *ehlorostannide*, $\text{AsMe}_2\text{SnCl}_2$, which forms large, colourless needles. By the action of phosphorus trichloride on the arsine, hydrogen chloride, cacodyl chloride, and a compound which is probably $(\text{CH}_3\text{P})_x$ or $(\text{CH}_3)_2\text{P}_4$ are produced. Arsenic trichloride reacts with dimethylarsine with formation of cacodyl chloride, hydrogen chloride, and the compound $(\text{CH}_3\text{As})_x$. When the arsine is heated with antimony trichloride, antimony hydride, hydrogen chloride, antimony, and cacodyl chloride are produced. By the action of the arsine on dibromosuccinic acid, cacodyl bromide and succinic acid are formed.

An improved method is described for the preparation of diphenylarsinic acid. Diphenylarsine, obtained by the reduction of diphenylarsinic acid, is a clear, colourless oil which boils at 174° under 25 mm. and at 155° under 37 mm. pressure; it is rapidly oxidised in the air with formation of diphenylarsinic acid and phenylcacodyl oxide. The *tribromide*, AsPh_2Br_3 , obtained by the action of bromine on the arsine, crystallises in golden-yellow plates, softens at 120° , melts at 129° , and is decomposed by water with formation of phenylcacodyl bromide. *Diphenylarsine iodide*, AsPh_2I , was obtained as an oil.

Basic diisoamylarsine chloride, $6\text{As}(\text{C}_5\text{H}_{11})_2\text{Cl} \cdot [\text{As}(\text{C}_5\text{H}_{11})_2]_2\text{O}$, obtained by the interaction of *isoamyl chloride* (2 mols.) and arsenic trichloride (1 mol.) in presence of sodium, is a colourless oil which boils at 263° under 750 mm. and at 148° under 33 mm. pressure, has a peculiar odour, and is soluble in the ordinary organic solvents, but insoluble in water; on distilling this compound, a small quantity of a white, soapy, solid substance is formed which is probably *isoamylcacodyl oxide*, $[\text{As}(\text{C}_5\text{H}_{11})_2]_2\text{O}$. By the action of bromine on *diisoamylarsine chloride*, the *chlorodibromide*, $\text{As}(\text{C}_5\text{H}_{11})_2\text{ClBr}_2$, is obtained, which forms white crystals, is soluble in ether or chloroform, and is slowly dissolved by water with formation of *isoamylarsinic acid*. When *diisoamylarsine chloride* is treated with hydrogen sulphide in presence of water, the *sulphide*, $[\text{As}(\text{C}_5\text{H}_{11})_2]_2\text{S}$, is produced, which crystallises in white needles, melts at $29-30^\circ$, is easily soluble in ether or carbon disulphide, sparingly so in alcohol, and insoluble in water. *isoAmylarsinic acid*, $(\text{C}_5\text{H}_{11})_2\text{AsO} \cdot \text{OH} \cdot 2\text{H}_2\text{O}$, forms large, flaky crystals, melts at $153-154^\circ$, and is easily soluble in alcohol, slightly so in water, and insoluble in ether. *Diisoamylarsine*, $\text{AsH}(\text{C}_5\text{H}_{11})_2$, obtained by the reduction of *diisoamylarsinic acid*, boils at 150° under 99 mm. pressure, and is oxidised by the air with formation of *diisoamylarsinic acid* and an oil which is probably *diisoamylcacodyl oxide*. E. G.

Preparation of Trialkyl-stibines, -arsines, and -phosphines by the Grignard Reaction. HAROLD HIBBERT (*Ber.*, 1905, **39**, 160—162. Compare Pfeiffer, *Abstr.*, 1905, i, 164; Auger and Billy, *ibid.*, 1904, i, 983).—Good yields (60—70 per cent.) of trimethylstibine may be obtained by the action of magnesium methyl iodide (3 mols.) on an ethereal solution of antimony trichloride cooled in ice and salt. When the product is distilled, the greater part of the stibine passes over with the ether, but the distillation is continued until the temperature of the oil-bath is 170°. Trimethylstibine is immediately thrown down in the form of the crystalline dibromide, SbMe_3Br_2 , on the addition of bromine.

The ethereal solution of trimethylarsine, when mixed with excess of bromine, yields the perbromide, AsMe_3Br_4 .

Triethylphosphine may be prepared by using a large excess of magnesium ethyl bromide. When the product is distilled, only 6 per cent. of the phosphine distils over with the ether, the larger portion distils over slowly when the oil-bath is at 160—200°. J. J. S.

[Grignard's Reaction with Dihaloids.] EDMOND E. BLAISE (*Bull. Soc. chim.*, 1906, [iii], **35**, 90—94).—The author claims that some of the observations given as new by Ahrens and Stapler (*Abstr.*, 1905, i, 423, 868) have previously been recorded by himself and others (*Abstr.*, 1901, i, 317; 1905, i, 111. Compare Zelinsky, *Abstr.*, 1903, i, 802, and Archibald and McIntosh, *Trans.*, 1904, **85**, 919). He also questions the probability of some of the conclusions drawn by the authors from these and other results contained in their memoirs on this subject. T. A. H.

Remarkable Difference in the Behaviour of Homologous Cyclic Molecules towards Ammonio-nickel Cyanide. KARL A. HOFMANN and H. ARNOLDI (*Ber.*, 1906, **39**, 339—344. Compare Hofmann and Höchtlen, *Abstr.*, 1903, i, 469).—Whilst benzene, aniline, and phenol interact with ammonio-nickel cyanide, as previously described (*loc. cit.*), the following substances are indifferent to the reagent: toluene, xylene, cumene, ψ -cumene, cymene, mesitylene, hexamethylbenzene, triphenylmethane, naphthalene, anthracene, phenanthrene, fluorene, diphenyl, triphenylmethane, triphenylcarbinol, styrene, amylene, ethylaniline, dimethylaniline, phenylhydrazine, *o*- and *p*-toluidine, anisole, *o*-cresol, nitrobenzene, fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, 2-methylpyridine, and quinoline.

Ammonio-nickel cyanide may be used to test for benzene in petroleum; Russian and American petroleum alone give no precipitate with the reagent, but do so on addition of benzene. When shaken with the reagent, piperidine forms a bluish-white precipitate, $\text{Ni}(\text{CN})_2 \cdot \text{C}_5\text{H}_5\text{N}$, which evolves pyridine, but not ammonia, when boiled with aqueous potassium hydroxide. Pyrrole forms a colourless, crystalline powder, $\text{Ni}(\text{CN})_2 \cdot \text{NH}_3 \cdot \text{C}_4\text{H}_5\text{N}$, which becomes brown on exposure to air and gives the pinewood reaction. Thiophen forms a violet-white, crystalline precipitate, $3\text{Ni}(\text{CN})_2 \cdot 3\text{NH}_3 \cdot \text{C}_4\text{H}_4\text{S}$. Furan forms a light violet-white, delicate crystalline precipitate, $\text{Ni}(\text{CN})_2 \cdot \text{NH}_3 \cdot \text{C}_4\text{H}_4\text{O}$.

A similar difference is shown by benzene and its homologues in their behaviour towards picric acid; this forms additive compounds with benzene and its higher homologues which are solid at or slightly below the ordinary temperature, but not with toluene, *m*-xylene, cumene, ψ -cumene, fluorobenzene, or chlorobenzene.

The benzene-picric acid compound decomposes completely in a few minutes in a vacuum at the ordinary temperature, whereas the benzene ammonio-nickel cyanide remains unchanged during four weeks in a vacuum at the ordinary temperature.

The interaction with ammonio-nickel cyanide appears to depend on the molecular volume of the compound, those which are precipitated having small molecular volumes at 15°: benzene, 88.6; aniline, 90.5; phenol, 88.8; pyridine, 80; pyrrole, 69.3; thiophen, 78.5; and furan, 72; whilst those which are not precipitated have large molecular volumes: toluene, 105.6; nitrobenzene, 103.6; iodobenzene, 110; bromobenzene, 105; chlorobenzene, 102; fluorobenzene, 93.8; *o*-toluidine, 107; *o*-cresol, 102; anisole, 109; phenylhydrazine, 97.6; α -methylpyridine, 97.6; quinoline, 117.8; and naphthalene, 111.

G. Y.

Chlorobenzenes as Solvents for Resins. L. E. ANDES (*Chem. Rev. Fett. Harz. Ind.*, 1906, 13, 32—33).—Chlorobenzene readily dissolves galipot (the resin obtained from *Pinus maritima*), colophony, mastic, asphalt, dammar, and metallic resinsates. These substances, with the exception of dammar, are also soluble in dichlorobenzene, whilst the following are insoluble in either solvent: shellac, sandarac, copals, benzoin, and amber. The inflammability of both solvents is very slight, they are miscible in all proportions with drying oils, turpentine, &c., and evaporate quickly. A good matt varnish is obtained by dissolving any resin in a mixture of alcohol and chlorobenzene.

W. P. S.

Bromination of Toluene. ARNOLD F. HOLLEMAN and F. H. VAN DER LAAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 512—518).—The authors have investigated quantitatively the influence of temperature, of light, and of bromine carriers on the action of bromine on an excess of toluene. The *o*- and *p*-bromotoluenes and the benzyl bromide formed by the reaction are estimated by the following method. After removal of hydrogen bromide and unchanged bromine by means of a current of air and by treatment with potassium iodide solution and of the excess of toluene by distillation, the benzyl bromide is estimated in a portion of the product by means of alcoholic silver nitrate, with which benzyl bromide interacts to form silver bromide quantitatively. The remainder of the product is shaken with dimethylaniline, washed with dilute nitric acid, dried, and distilled in a vacuum. The solidifying point of the distillate being determined, the amounts of *o*- and *p*-bromotoluene present are found to within 1 per cent. by reference to a solidifying point curve constructed from the results of determinations with mixtures of known composition.

Toluene is brominated in the dark at 25° only slowly, the reaction becoming more rapid as the temperature rises. The product obtained

at 25° contains 35.5, 53.9, and 10.6, at 50°, 23.5, 32.8, and 43.7, and at 75°, 6.2, 7.5, and 86.3 per cent. of *o*- and *p*-bromotoluenes and benzyl bromide respectively; the product formed at 100° consists wholly of benzyl bromide.

In diffuse daylight, the bromination proceeds rapidly at 25°, the reaction being completed in about ten minutes. If an excess of toluene is used, the product obtained at 25° contains 99.0, at 100° 99.5, per cent. of benzyl bromide, but if equivalent amounts of toluene and bromine are heated together at the boiling point of toluene, the product contains fractions which boil at higher temperatures.

The experiments with bromine carriers were carried out at 50° and in complete absence of light. The amounts of the carrier added are given in molecular proportion to each mol. of bromine used in the reaction.

With 0.0017, 0.0084, and 0.034 mol. of antimony tribromide, the product contains 22.4, 24.0, and 28.0 per cent. of *o*-bromotoluene, 33.4, 37.8, and 44.1 per cent. of *p*-bromotoluene, and 44.2, 38.2, and 27.9 per cent. of benzyl bromide respectively.

With 0.002, 0.004, 0.006, and 0.017 mol. of aluminium trichloride, the product contains 43.1, 0.5(i), 0, and 0 per cent. of benzyl bromide, the mixture of bromotoluenes consisting of 43.9, 44.6, 44.3, and 49.2 per cent. of the ortho- and 56.1, 55.4, 55.7, and 50.1 per cent. of the para-isomeride respectively.

With 0.0007, 0.001, and 0.002 mol. of ferric bromide, the product contains 40.8, 7.8, and 0 per cent. of benzyl bromide, whilst with 0.0007, 0.002, 0.006, and 0.01 mol. of this carrier the mixture of bromotoluenes contains 36.9, 36.0, 37.9, and 37.0 per cent. of the ortho- and 63.1, 64.0, 62.1, and 63.0 per cent. of the para-isomeride respectively.

On the other hand, with 0.02 mol. of phosphorus tribromide, the product contains 54.7 per cent. benzyl bromide, the mixture of bromotoluenes consisting of 41.4 and 58.6 per cent. of the ortho- and para-isomerides respectively. G. Y.

Ortho-substituted Iodo-compounds with Uni- and Multi-valent Iodine. CONRAD WILLGERODT and MAX SIMONIS (*Ber.*, 1906, 39, 269—280).—*m*-Nitro-*p*-tolyl iododichloride, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{ICl}_2$, prepared by passing dry chlorine into a well-cooled chloroform solution of *p*-iodo-*m*-nitrotoluene, crystallises in large, yellow, lustrous plates and decomposes at 71°; by aqueous sodium hydroxide, it is converted into *p*-iodoso-*m*-nitrotoluene, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{IO}$, which is a stable, intensely red powder exploding at 129°; the *acetate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{I}(\text{OAc})_2$, forms bright yellow, slender needles, and, when dry, explodes at 200°; the *basic sulphate*, $\text{C}_{14}\text{H}_{14}\text{O}_{10}\text{N}_2\text{I}_2\text{S}$, forms crystalline crusts and decomposes at 91°; the *basic nitrate*, $\text{C}_7\text{H}_7\text{O}_6\text{N}_2\text{I}$, melts and decomposes at 132°; the *basic iodide*, $\text{C}_7\text{H}_7\text{O}_6\text{NI}_2$, begins to decompose at 80°; the *basic chromate* explodes at 94° and the *formate*, $\text{C}_9\text{H}_8\text{O}_6\text{NI}$, at 72°.

p-Iodoxy-*m*-nitrotoluene, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{IO}_2$, prepared by decomposing the iodochloride with a solution of sodium hydroxide and sodium hypochlorite, crystallises from water or glacial acetic acid in long, slender, colourless needles and detonates at 196.5°.

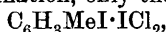
Di-m-nitro-p-tolyliodinium hydroxide is obtained in solution by the action of moist silver oxide on a mixture of *p*-iodoxy- and *p*-iodoso-m-nitrotoluene; the *iodide*, $\text{I}(\text{C}_6\text{H}_3\text{Me}\cdot\text{NO}_2)_2\text{I}$, crystallises from water in slender, colourless needles and decomposes at 51° .

Phenyl m-nitro-p-tolyliodinium hydroxide is prepared from iodoxy-benzene and *p*-iodoso-m-nitrotoluene in a similar manner.

p-Iodo-m-toluidine, prepared by heating *p*-iodo-m-nitrotoluene with freshly precipitated ferrous hydroxide and alcohol, crystallises from dilute alcohol, melts at 48° , and is nearly colourless. The *hydrochloride* forms pale yellow needles, the *nitrate* red needles, the *sulphate* is colourless; the *oxalate*, $2\text{C}_7\text{H}_8\text{NI}\cdot\text{H}_2\text{C}_2\text{O}_4$, melts at 113° . *p-Iodo-m-acetotoluidide* crystallises from acetic acid in slender, colourless needles and melts at $145\text{--}146^\circ$; *p-iodo-m-formotoluidide* is similar and melts at 129° .

On chlorinating *p*-iodo-m-toluidine in chloroform solution, a definite product cannot be isolated, but on similarly chlorinating *p*-iodo-m-acetotoluidide, 6-chloro-4-iodo-m-acetotoluidide is obtained; it crystallises from benzene or glacial acetic acid in fan-like aggregates of small, colourless needles, melts at $196\cdot5^\circ$, and combines with chlorine to form the *iododichloride*, $\text{NHAc}\cdot\text{C}_6\text{H}_2\text{MeCl}\cdot\text{ICl}_2$, which on warming loses chlorine and regenerates 6-chloro-4-iodo-m-acetotoluidide. On hydrolysis, the acetyl derivative gives 6-chloro-4-iodo-m-toluidine, which crystallises from dilute alcohol in thin, colourless plates, melts at 65° , and gives an *oxalate*, $\text{C}_{16}\text{H}_{16}\text{O}_4\text{Cl}_2\text{N}_2\text{I}_2$, crystallising in large plates and melting at 165° . On replacing the amino-group by chlorine, oxidising the 3:6-dichloro-4-iodotoluene so formed, and decomposing the dichloriodobenzoic acid, 1:4-dichloro-2-iodobenzene, melting at 20° , is obtained.

3:4-*Di-iodotoluene*, prepared from 4-iodo-m-toluidine through the diazo-reaction, crystallises from alcohol in flat, colourless needles and melts at $117\cdot5^\circ$. On chlorination, only the *monoiododichloride*,



is obtained, a di-iododichloride not being formed; attempts to convert this chloride into the corresponding iodoso- and iodoxy-compounds were without successful issue. W. A. D.

Certain Derivatives of Benzenesulphonylaminoacetonitrile. TREAT B. JOHNSON and ELMER V. MCCOLLUM (*Amer. Chem. J.*, 1906, 35, 54—67).—Benzenesulphonylaminoacetonitrile (Knoevenagel and Lebach, *Abstr.*, 1904, i, 994) may be prepared by treating aminoacetonitrile with benzenesulphonic chloride; it melts at 80° .

By the action of methyl iodide on the silver derivative of this compound, *benzenesulphonylmethylaminoacetonitrile*, $\text{SO}_2\text{Ph}\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{CN}$, is obtained, which crystallises from water in plates, melts at 97° , and is readily hydrolysed by hydrochloric acid. *Benzenesulphonylmethylaminoacetic acid*, $\text{SO}_2\text{Ph}\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, crystallises from hot water in prisms and melts at 179° ; its *ethyl* ester boils at $215\text{--}216^\circ$ under 15 mm. pressure. When this acid is boiled with hydrochloric acid for fifteen hours, sarcosine benzenesulphonate is obtained.

Benzenesulphonylethylaminoacetonitrile, $\text{SO}_2\text{Ph}\cdot\text{NEt}\cdot\text{CH}_2\cdot\text{CN}$, boils and suffers partial decomposition at $225\text{--}235^\circ$ under 21 mm. pressure;

the corresponding *acid* crystallises from water in colourless plates and melts at 116° .

Benzenesulphonyl-n-propylaminoacetonitrile was obtained as an oil which, on hydrolysis, yielded the corresponding *acid*, which crystallises in stout prisms and melts at $99-101^{\circ}$.

Benzenesulphonylcarbethoxyaminoacetonitrile,
 $\text{SO}_2\text{Ph}\cdot\text{N}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{CN}$,

obtained by the action of ethyl chloroformate on the potassium derivative of benzenesulphonylaminoacetonitrile, crystallises from alcohol in needles, melts at $83-85^{\circ}$, and when heated with solution of sodium hydroxide and afterwards acidified with hydrochloric or sulphuric acid, is reconverted into benzenesulphonylaminoacetonitrile.

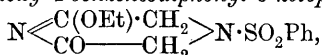
Benzenesulphonylbenzylaminoacetonitrile forms colourless prisms and melts at $68-70^{\circ}$; the corresponding *acid* crystallises in needles and melts at $123-125^{\circ}$.

Benzenesulphonyl-p-nitrobenzylaminoacetonitrile crystallises in prisms and melts at $123-125^{\circ}$; the *acid* forms hair-like needles and melts and decomposes at $210-212^{\circ}$.

Ethyl benzenesulphonylcyanomethylaminoacetate,
 $\text{SO}_2\text{Ph}\cdot\text{N}(\text{CH}_2\cdot\text{CN})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$,

obtained by the action of ethyl chloroacetate on benzenesulphonylaminoacetonitrile, crystallises in radiating needles and melts at $68-70^{\circ}$. When this ester is warmed with solution of sodium hydroxide until it has completely dissolved and is subsequently acidified with hydrochloric or sulphuric acid, 2:6-diketo-4-benzenesulphonyl-piperazine, $\text{NH}\begin{smallmatrix} \text{CO}\cdot\text{CH}_2 \\ \text{CO}\cdot\text{CH}_2 \end{smallmatrix}\text{N}\cdot\text{SO}_2\text{Ph}$, is produced, which crystallises in

prisms, melts and decomposes at $198-199^{\circ}$, and when heated with strong hydrochloric acid in a sealed tube for two hours at $140-150^{\circ}$ is converted into iminodiacetic acid, which melts and decomposes at $235-236^{\circ}$. 2-Ethoxy-4-benzenesulphonyl-6-ketopiperazine,



obtained by the action of ethyl iodide on the silver derivative of 2:6-diketo-4-benzenesulphonylpiperazine, crystallises in pyramids and melts at $130-132^{\circ}$.

Benzenesulphonylbenzoylaminoacetonitrile, $\text{SO}_2\text{Ph}\cdot\text{NBz}\cdot\text{CH}_2\cdot\text{CN}$, forms radiating needles, melts at $110-112^{\circ}$, and when boiled with concentrated hydrochloric acid is converted into a mixture of benzoic and benzenesulphonylaminoacetic acids. Phosphorus pentachloride reacts with benzenesulphonylaminoacetic acid with formation of benzenesulphonylaniline.

Carbethoxyaminoacetonitrile, $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CN}$, obtained by the action of ethyl chloroformate on the sulphate of aminoacetonitrile in presence of sodium hydroxide, boils at 175° under 35 mm. pressure, crystallises in radiating prisms, and melts at $48-50^{\circ}$.

An attempt was made to effect the condensation of benzenesulphonylaminoacetic acid with catechol, but without success. E. G.

Molecular Compounds of Nitro-compounds with Amines.

EMILIO NOELTING and E. O. SOMMERHOFF (*Ber.*, 1906, 39, 76-79. Compare Hepp, *Abstr.*, 1883, 315; van Romburgh, *Abstr.*, 1895, i,

652; Sudborough, *Trans.*, 1901, 79, 522; Sachs and Steinert, *Abstr.*, 1904, i, 506).—The authors have prepared a number of *additive compounds* from 1 mol. of trinitrobenzene with 1 mol. of each of the amines mentioned below. The colours and crystalline forms are those of the additive compounds; the temperatures given are the melting points.

o-Toluidine: light red needles, 125—127°; *m*-toluidine: light red needles, 93°; *p*-toluidine: dark red needles, easily decomposed; *o*-3-xylydine: red needles, 125—128°; *m*-4-xylydine: brownish-red needles, 96—98°; *m*-2-xylydine: light red needles, 118—120°; *p*-xylydine: red needles, 100—101°; mesidine: brownish-red needles, 120—122°; ψ -mesidine: dark brownish-red needles, 108—110°; 5-*tert*-butyl-*m*-2-xylydine: brown needles, 120—122°; benzidine: black needles; tolidine: black needles, 178°; dimethyl-*p*-toluidine: black needles, 124°; *o*-phenylenediamine: brown needles, 175°; *m*-phenylenediamine: brown needles; *p*-phenylenediamine: blackish-brown needles; *m*-tolylene-diamine: brown needles; *m*-xylylene-4:6-diamine: blackish-brown needles; 4-amino-1-toluquinoline: black needles; tetrahydroquinoline: dark red needles.

Aromatic diamines do not form additive compounds with 2 mols. of trinitrobenzene. Additive compounds are not formed by trinitrobenzene with *p*-bromoaniline, bromo-*m*-xylydine, azobenzene, or the nitro-*o*-toluidines. The following amines form *additive* compounds with 2 mols. of trinitrobenzene:

Diphenylamine: glistening, black plates, 109—110°; *p*-ditolylamine: glistening, black plates; quinoline: white needles, readily decomposed; 1:2-xyloquinoline: long, white needles, 113°.

The *additive* compounds of 1 mol. of trinitrotoluene with 1 mol. of the following amines are formed less readily and are less stable than the additive compounds of trinitrobenzene:

o-Toluidine: light red needles, 53—55°; *m*-toluidine: light red needles, 62—63°; *m*-4-xylydine: red needles, 43—45°; ψ -cumidine: stable, brown needles; dimethyl-*p*-toluidine: bluish-black needles.

When mixed in molecular proportions in alcoholic solution at the laboratory temperature, trinitrobenzoic acid and ψ -cumidine form a colourless *salt*, which, when warmed, loses carbon dioxide and yields the red additive compound of trinitrobenzene and ψ -cumidine. But when heated together in methyl-alcoholic solution on the water-bath, trinitrobenzoic acid and ψ -cumidine form a brown *additive compound*, which melts at 140—143° and dissolves in warm hydrochloric acid to form a red solution. The basic component of this compound can be titrated with sodium nitrite solution.

With freshly distilled, colourless aniline, nitrobenzene, *p*-nitro-toluene, and *m*-dinitrobenzene give intense red colorations which disappear on adding alcohol.

G. Y.

Formation of Anilides. HEINRICH GOLDSCHMIDT and ROBERT BRÄUER (*Ber.*, 1906, 39, 97—108. Compare Goldschmidt and Wachs, *Abstr.*, 1898, ii, 67).—Experiments with aniline or *o*-toluidine and *n*-butyric or *isobutyric* acid at 100° show that the formation of the anilide is a reaction of the second order, whereas on addition of picric

acid it becomes unimolecular. The rate of formation of the anilides and *o*-toluidides, with or without the addition of picric acid, diminishes for the four acids investigated, in the order: acetic, propionic, *n*-butyric, and isobutyric acid.

As the reaction between formic acid and aniline at 100° is completed in a few minutes, the experiments with this acid and aniline or *o*-toluidine were carried out at 45–55°. As with the above-mentioned aliphatic acids, the reaction is bimolecular, but on addition of picric acid an increase in the velocity of the reaction is observed only if the concentration of the catalyst is not less than that of the formic acid. It may be that in the formation of anilides in presence of a catalytic agent the two reactions of the first and second orders, respectively, take place together, in which case the velocity of the whole reaction is represented by the equation: $\frac{dx}{dt} = k(a-x)c + k'(a-x)^2$, in which k and k' are products of the velocity constants with the constants of equilibrium which determine the different states in which the aliphatic acid exists in the basic solvent.

The reaction between formic acid and aniline in presence of picric acid does not stop at the formation of the anilide, but proceeds to that of diphenylformamidine. G. Y.

Kinetics of the Fission of Carbon Dioxide from Trichloroacetic Acid in Aniline Solution. HEINRICH GOLDSCHMIDT and ROBERT BRÄUER (*Ber.*, 1906, 39, 109–112. Compare preceding abstract; Silberstein, *Abstr.*, 1885, 160; Balcom, *Inaug. Diss.*, Heidelberg, 1905).—Contrary to the behaviour of acetic acid and its homologues with aniline, the interaction of trichloroacetic acid and aniline at 25–45° is unimolecular, and leads to the formation of carbon dioxide and chloroform. The velocity of the reaction is influenced to only a slight extent by the addition of strong acids; thus the value of k for the reaction in presence of picric acid at 25° is slightly greater than the value obtained without addition of picric acid, whilst at 45° the two values of k are identical. G. Y.

Action of Hydrogen Peroxide on Sulphuric Acid Solutions of Diphenylamine. A. USCHAKOFF (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 913–915).—The action of a solution of hydrogen peroxide on a concentrated sulphuric acid solution of diphenylamine yields: (1) the compound $C_{24}H_{20}O_2N_2$, which is soluble in 5 per cent. potassium hydroxide solution and also in concentrated sulphuric acid, to which it imparts a blue colour; on reduction with zinc dust and acetic acid or with sodium and alcohol, diphenylamine is not formed, but the violet colour of the solution changes to pale yellow, which, in presence of air or water, again becomes violet; (2) the compound $C_{60}H_{49}O_2N_5$, which is an amorphous, violet powder, melting at above 100°; with sulphuric acid, it behaves like compound (1), and when heated with zinc dust it yields a small proportion of diphenylamine, certain oily products, and from 10 to 20 per cent. of a compound crystallising from ethyl acetate in silvery, hexagonal plates which melt at 240°. T. H. P.

Diphenylamine Nitrates. A. USCHAKOFF (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 911—912).—The salt $3\text{NHPh}_2, 2\text{HNO}_3$ forms well-developed crystals melting at $102\text{--}103^\circ$ and dissolves in alcohol, ether, aniline, or acetic acid; it is decomposed by boiling water and turns blue in the air. The salt $4\text{NHPh}_2, \text{HNO}_3$ has the melting point 54° , the same as diphenylamine itself, indicating that it decomposes before melting.

T. H. P.

Terpenes and Ethereal Oils. LXXV. Conversion of Ketones and Aldehydes into Bases. OTTO WALLACH [with KARL HÜTTNER and JOHANNES ALTENBURG] (*Annalen*, 1905, **343**, 54—74).—The conversion of ketones and aldehydes into bases by treatment with ammonium formate is represented as follows: $\text{COR}_2 + \text{NH}_3 = \text{OH}\cdot\text{CR}_2\cdot\text{NH}_2$; $\text{OH}\cdot\text{CR}_2\cdot\text{NH}_2 + \text{HCO}_2\text{H} = \text{CHR}_2\cdot\text{NH}_2 + \text{CO}_2 + \text{H}_2\text{O}$, the free formic acid acting as a reducing agent. This view of the reaction accounts for the fact that secondary and tertiary bases are formed with the primary base; the primary base reacts with the aldehyde or ketone in the place of the ammonia. Since the reaction depends on the base being free and uncombined with acids, the presence of acids affects the course of the reaction. Generally under the conditions at which these reactions occur, the salts of the primary bases are less dissociated than ammonium salts, and hence the reaction between ammonia and the aldehyde or ketone predominates, but small amounts of secondary (or tertiary) bases are then produced.

It has been found (i) that the addition of anhydrous formic or acetic acid to the mixture of the ammonium formate and aldehyde or ketone leads to a single product, the primary amine; (ii) that the reaction will take place at a low temperature, and accordingly the formation of formyl derivatives is avoided; aromatic bases form such derivatives at any temperature at which the reaction will take place. (iii) The reaction can be used with all ketones and aldehydes and all classes of bases, and can thus be used in the preparation of mixed secondary and tertiary bases.

Diethylmethylamine [γ -aminopentane], $\text{CHEt}_2\cdot\text{NH}_2$, was prepared from diethyl ketone and ammonium formate, the two substances being boiled together in the presence of a little acetic acid. *Formyl- α -phenylethylamide*, $\text{CHMePh}\cdot\text{N}\cdot\text{OCH}$, was prepared from acetophenone and ammonium formate at 155° , and is an oil boiling at 200° under 14 mm. pressure; in the presence of acetic acid, α -phenylethylamine is obtained. *cycloHexanone* and ammonium formate in the presence of acetic acid yield mainly dicyclohexylamine, $\text{NH}(\text{C}_6\text{H}_{11})_2$, which is a liquid boiling at $251\text{--}252^\circ$, and has a sp. gr. 0.925 and n_D 1.4861 at 18° ; the nitrate, oxalate, and thiocyanate are sparingly soluble; the *nitrosoamine*, $\text{N}(\text{C}_6\text{H}_{11})_2\cdot\text{NO}$, is characteristic and melts at $105\text{--}106^\circ$. *Benzylcyclohexylamine*, $\text{C}_6\text{H}_{11}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$, prepared by boiling for four hours *cyclohexanone*, benzylamine, and formic acid, is a colourless liquid boiling at $281\text{--}282^\circ$; its *formyl* derivative is produced at the same time.

1-Methylcyclohexane-3-one and ammonium formate in the presence of acetic or formic acid yield the secondary base, *di-1-methylcyclohexyl-3-amine*, $\text{NH}(\text{C}_6\text{H}_{10}\text{Me})_2$, which boils at $134\text{--}135^\circ$ under 12—14 mm.

and at 273° in an atmosphere of hydrogen under the ordinary pressure ; it has a sp. gr. 0.8878 and n_D 1.4756 at 21° ; the base appears to be a mixture of stereoisomeric compounds. The same mixture can be obtained by heating together the methylcyclohexanone and methylhexylamine formate and formic acid.

Amylamine and the methylcyclohexanone in the presence of formic acid give 1-methylcyclohexylamylamine, $C_5H_{11} \cdot NH \cdot C_6H_{10}Me$, which boils at 234° . 1-Methylcyclohexanone-3 and benzylamine yield benzyl-1-methylcyclohexyl-3-amine, $C_6H_{10}Me \cdot NH \cdot CH_2Ph$, which boils at $165-170^{\circ}$ under 12 mm. pressure and has a sp. gr. 0.946 and n_D 1.5182 at 22° .

Triisoamylamine is formed from valeraldehyde, ammonium formate, and formic acid, and tribenzylamine from benzaldehyde and ammonium formate and formic acid. Valeraldehyde and aniline formate give formanilide and diamylaniline, $NPh(C_5H_{11})_2$, which boils at $264-265^{\circ}$. Methylamylaniline is obtained from valeraldehyde and methylaniline formate.

At low temperatures, benzaldehyde and aniline formate yield benzylaniline, $CH_2Ph \cdot NHPh$, which melts at 32° and yields a nitrosoamine melting at 57° . Formylbenzylanilide, which is mainly produced at higher temperatures, melts at 48° .

Methylcyclohexylamine formate and benzaldehyde in the presence of formic acid yield, at 160° , the same benzylmethylcyclohexylamine which is formed in the interaction of methylhexanone and cyclohexylamine. Benzaldehyde and ethylamine formate give benzylethylamine, and with piperidine formate, benzylpiperidine boiling at 248° .

K. J. P. O.

Asymmetric Nitrogen. XXII. Optically Active Ammonium Salts. EDGAR WEDEKIND (*Ber.*, 1906, 39, 474—480. Compare this vol., i, 14).—*l*-Phenylbenzylmethylpropylammonium iodide and *l*-phenylbenzylmethylisobutylammonium iodide respectively were examined crystallographically, and no hemihedrisism was detected in either case. *l*-Phenylbenzylmethylpropylammonium bromide, prepared by the addition of potassium bromide to a solution of *l*-phenylbenzylmethylpropylammonium *d*-bromocamphorsulphonate, when crystallised either from water or from alcohol also shows no tendency to hemihedrisism ; the specimen which was crystallised from water was isomorphous with the iodide described, whilst the specimen crystallised from alcohol had a different crystalline form.

The tendency to autoracemisation exhibited by various optically active ammonium salts investigated by the author in chloroform solution is characteristic with the chlorides, bromides, and iodides ; the nitrates, however, are optically stable. *d*-Phenylbenzylmethylpropylammonium nitrate, prepared by the addition of silver nitrate to an alcoholic solution of the *d*-iodide, forms colourless crystal and decomposes at 170° ; it has $[\alpha]_D +114^{\circ}$ in chloroform solution, a value which exhibited practically no variation when the solution remained at the laboratory temperature for two days. Solutions of the corresponding chloride, bromide, and iodide respectively all exhibited autoracemisation, the phenomenon being more marked with the iodide than with

the bromide. The fluoride does not appear to undergo any marked autoracemisation. The free base, *l*-phenylbenzylmethylisobutylammonium hydroxide, undergoes autoracemisation in chloroform solution more slowly than does its iodide.

A. McK.

Asymmetric Nitrogen. XXIII. Isomerism with Asymmetric Ammonium Salts. EDGAR WEDEKIND (*Ber.*, 1906, 39, 481—488. Compare preceding abstract).—Whilst *o*-methoxyphenylbenzylmethylallylammonium iodide may be prepared from benzyl iodide and methylallyl-*o*-anisidine or from allyl iodide and benzylmethyl-*o*-anisidine, the product obtained from methyl iodide and benzylallyl-*o*-anisidine consists of anisyltrimethylammonium iodide. This observation, taken in conjunction with the results obtained by Jones (*Trans.*, 1905, 87, 1721), led the author to re-examine the case of isomerism which he thought he had discovered with phenylbenzylmethylallylammonium iodide; the so-called " β -iodide" is now shown to be phenylbenzyltrimethylammonium iodide, which decomposes at 164—165°. The analyses, formerly made by the author with the " β -iodide," were made with a mixture of phenylbenzyltrimethylammonium iodide and the normal phenylbenzylmethylallylammonium iodide. Optically inactive isomerides of phenylbenzylmethylallylammonium iodide accordingly do not exist.

[With EMANUEL FRÖHLICH].—*Methylallyl-o-anisidine*, prepared from allyl iodide and methyl-*o*-anisidine, is a yellow oil which boils at 167° under 85 mm. pressure; its *picrate* melts at 139°.

Benzylmethyl-o-anisidine, prepared from benzyl bromide and methyl-*o*-anisidine, is a viscid, yellow oil which boils at 217—220° under 65 mm. pressure; its *picrate* melts at 129°.

Benzyl-o-anisidine, prepared from benzyl chloride and *o*-anisidine or from benzyl chloride, *o*-anisidine, and potassium hydroxide, is a viscid, yellow oil which boils at 217—220° under 25 mm. pressure; its *picrate* melts at 137°.

Benzylallyl-o-anisidine, prepared from allyl iodide, benzyl-*o*-anisidine, and potassium hydroxide, boils at 205—206° under 50 mm. pressure.

o-Methoxyphenylbenzylmethylallylammonium iodide, prepared from benzyl iodide and methylallyl-*o*-anisidine, is identical with the compound obtained from allyl iodide and benzylmethyl-*o*-anisidine and decomposes at 120°.

Anisyltrimethylammonium iodide, obtained from methyl iodide and benzylallyl-*o*-anisidine, decomposes and sublimes at about 210—220°.

A. McK.

Certain Nitrogen Compounds. ANGELO ANGELI and VINCENZO CASTELLANA (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 657—660).—Angeli and his collaborators have shown (*Abstr.*, 1905, i, 873) that, in the form of salts, nitrosophenylhydroxylamine, $\text{NO}\cdot\text{NPh}\cdot\text{OH}$, and phenylnitroamine (phenylnitroamic acid), $\text{NPh}\cdot\text{NO}_2$, have the structures $\text{O}\cdot\text{NPh}\cdot\text{N}\cdot\text{OH}$ and $\text{NPh}\cdot\text{NO}\cdot\text{OH}$ respectively. These differ as regards the position which the oxygen atom takes up in the diazobenzene hydroxide, $\text{NPh}\cdot\text{N}\cdot\text{OH}$, from which they are derived. Since some authorities ascribe the structure $\text{O} \leq \overset{\text{NPh}}{\text{N}} \cdot \text{OH}$ to phenylnitroamic

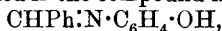
acid, it is seen that this substance stands in very close relationship to the aromatic azoxy-compounds, which contain the ring $\cdot\text{N}-\text{N}\cdot$



united to two radicles, generally identical. Asymmetric or mixed azoxy-compounds, $\text{R}(\text{N}_2\text{O})\text{R}'$, which are very difficult to prepare, should exist in only one modification if they contain the N_2O ring, whilst if their constitution is analogous with that of nitrosophenylhydroxylamine two isomerides should be possible.

By condensing nitrobenzene and aniline, the authors have obtained, besides azoxybenzene, a brownish-red oil which does not reduce Fehling's solution, is decomposed by hydrochloric acid into nitrobenzene and aniline, and is probably a condensation product of the formula $\text{O}:\text{NPh}(\text{OH})\cdot\text{NHPh}$. Nitrobenzene reacts in a similar way with *p*-toluidine.

To the condensation products of aldehydes with substituted hydroxylamines, Bamberger attributes a structure, $\text{O} \begin{array}{c} \text{CHR} \\ | \\ \text{NR} \end{array}$, analogous with that of the azoxy-compounds. The authors find that the product obtained from benzaldehyde and phenylhydroxylamine forms an additive *compound*, melting at 170° , with 1 mol. of phenylcarbimide, a fact which is best explained if the compound has the structure



since this does not require intramolecular change to be effected by the phenylcarbimide. Confirmation of this conclusion is obtained in the behaviour of phenylhydroxylamine, which combines with 1 mol. of phenylcarbimide to give a *compound*, melting at 126° , soluble in alkali, and capable of reducing Fehling's solution, the reduction being accompanied by the odour of nitrosobenzene. Phenylcarbimide does not, therefore, determine the transposition of phenylhydroxylamine into *p*-aminophenol, since, if this were effected, two molecules of the carbimide should participate in the reaction and no odour of nitroso-compound should be observed.

T. H. P.

Action of Carbamide on Compounds of Cyanoacetic Acid.

GUSTAV FRERICHs and L. HARTWIG (*J. pr. Chem.*, 1906, [ii], 73, 21—48. Compare this vol., i, 74).—When heated with aniline over a naked flame, the ethyl ester, $\text{C}_6\text{H}_5\text{O}_3\text{N}_2$, melting at 162° (*loc. cit.*), yields *s*-diphenylcarbamide, a small quantity of *s*-diphenylbiuret, and a dibasic acid, $\text{C}_{30}\text{H}_{24}\text{O}_3\text{N}_6$, which forms white leaflets, melts at 195° , and gives an intense red coloration with alcoholic ferric chloride. The action of aniline on the methyl ester, $\text{C}_5\text{H}_6\text{O}_3\text{N}_2$, melting at 128° (*loc. cit.*), leads to the formation of the same products. The sodium, potassium, and silver salts of the dibasic acid were analysed; its diethyl ester, $\text{C}_{30}\text{H}_{22}\text{O}_3\text{N}_6\text{Et}_2$, formed by the action of ethyl iodide and alcoholic potassium hydroxide on the acid, crystallises in white needles and melts at 158° ; the dibenzyl ester, $\text{C}_{30}\text{H}_{22}\text{O}_3\text{N}_6(\text{CH}_2\text{Ph})_2$, crystallises in white needles and melts and decomposes at 215° . When hydrolysed with concentrated hydrochloric acid or with 10 per cent. aqueous

potassium hydroxide, the dibasic acid yields ammonia and aniline; no other organic substance could be detected amongst the products of the hydrolysis.

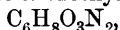
When heated with *p*-toluidine, the ethyl ester, $C_6H_8O_3N_2$, forms *p*-tolylcarbamide, *s*-di-*p*-tolylcarbamide, and a dibasic acid, $C_{33}H_{30}O_3N_6$, which crystallises in white leaflets, melts at 221° , and gives a red coloration with alcoholic ferric chloride.

With *m*-toluidine, the ethyl ester, $C_6H_8O_3N_2$, yields *m*-tolylcarbamide, *s*-di-*m*-tolylcarbamide, and a dibasic acid, $C_{33}H_{30}O_3N_6$, which crystallises in glistening, colourless leaflets, melts at 186° , and gives a red coloration with alcoholic ferric chloride.

The dibasic acid, $C_{30}H_{21}O_3N_6Cl_3$, formed by heating the ethyl ester, $C_6H_8O_3N_2$, with *m*-chloroaniline, is obtained as a crystalline powder melting at 217° . When treated with benzyl chloride and alcoholic potassium hydroxide, it yields the *dibenzyl* ester, $C_{30}H_{19}O_3N_6Cl_2(CH_2Ph)_2$, which crystallises in needles, melts at 186 — 188° , and is insoluble in aqueous ammonia or dilute alkali hydroxides.

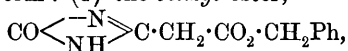
When heated with *m*-bromoaniline, the ethyl ester, $C_6H_8O_3N_2$, yields a mixture of *m*-bromophenylcarbamide and *s*-di-*m*-bromophenylcarbamide and the dibasic acid, $C_{30}H_{21}O_3N_6Br_3$, which is obtained on acidification of its ammoniacal solution as a white, crystalline powder, and when heated with benzyl chloride and alcoholic potassium hydroxide on the water-bath forms the *dibenzyl* ester, $C_{30}H_{19}O_3N_6Br_3(CH_2Ph)_2$; this crystallises in white needles and melts at 185 — 187° .

When heated with an excess of methylaniline, the ethyl ester,



yields (1) its ammonium salt; this must be due to partial decomposition of the acid, yielding cyanic acid, which interacts with methylaniline to form *s*-diphenyldimethylcarbamide and ammonia; and (2) a dibasic acid, $C_{33}H_{30}O_3N_6$, which forms thick, yellow, rhombic crystals, melts at 175° , and gives a red coloration with alcoholic ferric chloride. The same products are obtained by the action of methylaniline on the methyl ester, $C_5H_6O_3N_2$.

The ethyl ester, $C_6H_8O_3N_2$, interacts with an excess of warm benzyl alcohol to form: (1) the *benzyl* ester,



which crystallises from dilute alcohol in colourless octahedra or broad, flat, denticulate aggregates and melts and decomposes at 148° , and (2) a substance, $C_{17}H_{13}O_5N$, which crystallises in flat, white needles, melts at 267° , and with ferric chloride in aqueous solution forms a reddish-violet precipitate which dissolves in alcohol, forming a dark red solution which gradually deposits dark violet prisms.

When heated at 180° , the ethyl ester, $C_6H_8O_3N_2$, melts and evolves at first alkaline, but later acid, vapours having an odour of ethyl cyanoacetate; the distillate gives the iodoform reaction. The residue consists of a white, crystalline powder, $C_8H_7O_4N_3$ (?), which decomposes at high temperatures, becoming yellow and finally black; it is soluble in aqueous ammonia, from its solution in which it is reprecipitated by addition of hydrochloric acid; it does not give the murexide reaction and does not give the reaction products of cyanic acid when

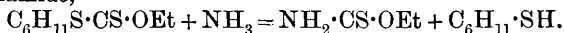
heated with aniline, but yields bromoform and ammonium bromide when treated with bromine water.

When heated with carbamide, cyanoacetic acid forms cyanoacetyl-carbamide, or, on prolonged heating, uric acid (compare Formánek, Abstr., 1892, 149). A number of experiments intended to throw light on the mechanism of this reaction yielded only negative results. G. Y.

Hexahydrothiophenol (*cycloHexyl Mercaptan*). WALTHER BORSCHKE and W. LANGE (*Ber.*, 1906, 39, 392—397. Compare Abstr., 1905, i, 766).—The yield of *cyclohexyl hydrosulphide* obtained by reducing *cyclohexanesulphonic chloride* with tin and hydrochloric acid is some 40—50 per cent. of the theoretical. Only a small amount of the mercaptan is formed when *cyclohexyl bromide* is heated with an alcoholic solution of potassium hydrogen sulphide, the chief product being *cyclohexene*

cycloHexyl xanthate, $C_6H_{11}S \cdot CS \cdot OEt$, is obtained as a yellow oil distilling at 150—153° under 16 mm. pressure when *cyclohexyl bromide* is warmed with an alcoholic solution of potassium xanthate. A small amount of *cyclohexyl trithiocarbonate*, $CS(S \cdot C_6H_{11})_2$, is also formed. It crystallises from alcohol in yellow needles and melts at 75—76°.

Ammonia converts *cyclohexyl xanthate* into *cyclohexyl mercaptan* and xanthamide,



The mercaptan is a colourless oil distilling at 158—160° and is lighter than water. The *mercuric* compound, $C_6H_{11}S \cdot HgCl$, is obtained as a white precipitate on the addition of an alcoholic solution of mercuric chloride to the mercaptan dissolved in alcohol. *cycloHexyl methyl sulphide*, $C_6H_{11} \cdot SMe$, is a colourless oil distilling at 179—180°. *cycloHexyldimethylsulphonium iodide*, $C_6H_{11}SMe_2I$, forms small crystals melting at 102°. It is deliquescent and dissolves readily in methyl or ethyl alcohol, but only sparingly in ether. The corresponding *hydroxide*, $C_6H_{11} \cdot SMe_2 \cdot OH$, melts at about 80°, the *chloride* at about 90°, and the *platinichloride*, $(C_6H_{11}SMe_2)_2PtCl_6$, at 136°. The last compound crystallises from water in brick-red needles. J. J. S.

[4-Nitro-2-amino-6-acetylaminophenol.] LEOPOLD CASSELLA & Co. (D.R.-P. 161341).—Acetic anhydride reacts with sodium picramate at 60° to form sodium acetylpicramate, which is reduced by sodium sulphide at 80°, and acids then precipitate 4-nitro-2-amino-6-acetylaminophenol, sparingly soluble in alcohol, more readily in ether or acetic acid. Acids hydrolyse it to 4-nitro-2:6-diaminophenol. The diazonium compound forms sparingly soluble yellow crystals and may be used for the preparation of azo-dyes. C. H. D.

Nitration of Benzoyl- and Dibenzoyl-*p*-aminophenol. FREDERIC REVERDIN and ERNEST DELÉTRA (*Ber.*, 1906, 39, 125—129. Compare Reverdin and Dresel, Abstr., 1905, i, 51, 430).—2:6-Dinitro-4-benzoylaminophenol, $NHBz \cdot C_6H_2(NO_2)_2 \cdot OH$, is formed by the action on *p*-benzoylaminophenol of a mixture of concentrated sulphuric acid and nitric acid of sp. gr. 1.4 at 7—12°, or of nitric acid of sp. gr. 1.5 at -10—0°, or of nitric acid of sp. gr. 1.34 at 20—26°. It crystallises from acetone in golden leaflets, melts at 263°, and when heated with

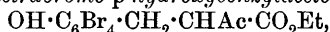
concentrated sulphuric acid on the water-bath is hydrolysed with formation of *isopicramic acid*. The *acetyl* derivative crystallises in yellowish-brown needles or brown prisms and melts at 180° . When reduced with zinc and hydrochloric acid, 2:6-dinitro-4-benzoylamino-phenol yields *p*-triaminophenol and benzoic acid.

The action of nitric acid of sp. gr. 1.4 on dibenzoyl-*p*-aminophenol (a) in concentrated sulphuric acid at $7-14^{\circ}$ leads to the formation of 2:6-dinitro-4-benzoylamino-phenol, melting at 263° ; (b) in a mixture of concentrated sulphuric acid and acetic anhydride at $6-11^{\circ}$ leads to the formation of dinitro-*p*-nitrobenzoylamino-phenyl nitrobenzoate, melting at 229° ; or (c) in a mixture of concentrated sulphuric acid and glacial acetic acid to the formation of 3-nitro-4-benzoylamino-phenyl benzoate, melting at 147° . G. Y.

Tetrabromo-*p*-cresol ψ -Bromide. XV. THEODOR ZINCKE and K. BÖTTCHER (*Annalen*, 1905, 343, 100—129. Compare this vol., i, 172).—This communication is an extension of the research on the same subject previously published (*Abstr.*, 1902, i, 284). The results are in agreement with the views expressed by Auwers (*Abstr.*, 1902, i, 217), and, in consequence, the formulæ previously suggested are now somewhat modified.

*Octabromo-*p*-diphenolmethane*, $\text{CH}_2(\text{C}_6\text{Br}_4\cdot\text{OH})_2$, prepared by dissolving tetrabromo-*p*-cresol ψ -bromide in 5 per cent. sodium hydroxide or by heating tetrabromo-*p*-hydroxybenzyl alcohol at 200° , crystallises in needles or leaflets melting at $280-281^{\circ}$; its *acetyl* derivative crystallises in needles melting at $278-279^{\circ}$.

*Tetrabromo-*p*-hydroxybenzylacetone*, $\text{OH}\cdot\text{C}_6\text{Br}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$, prepared from the ψ -bromide by the action of alkali hydroxide in acetone solution, crystallises in colourless needles melting at $175-176^{\circ}$; its sodium salt forms scales and its *acetyl* derivative needles melting at $181-182^{\circ}$. *Ethyl tetrabromo-*p*-hydroxybenzylacetate*,

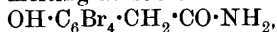


prepared by boiling a mixture of ethyl sodioacetoacetate and tetrabromo-*p*-cresol ψ -bromide in benzene solution, crystallises in needles melting at $117-118^{\circ}$, and is converted into the acetone derivative just described by boiling with a solution of barium hydroxide.

*Tetrabromo-*p*-hydroxybenzylaniline*, prepared from the tetrabromo- ψ -bromide and aniline (2 molecules), crystallises in needles melting at $120-122^{\circ}$. The corresponding *tetrabromo-*p*-hydroxyphenylacetone nitrile*, prepared from the tetrabromo- ψ -bromide and potassium cyanide, crystallises in needles melting at $214-216^{\circ}$; by dilute sulphuric acid, it is hydrolysed to the corresponding acid, and by nitric acid it is oxidised to a ψ -quinol and oxalic acid. Its *acetyl* derivative forms crystals melting at $183-184^{\circ}$.

The *quinol*, $\text{CO}\left\langle\begin{smallmatrix}\text{CBr}\cdot\text{CBr} \\ \text{CBr}\cdot\text{CBr}\end{smallmatrix}\right\rangle\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{CN}$, prepared from the nitrile, crystallises in yellow needles or prisms melting at $209-211^{\circ}$. *Tetrabromo-*p*-hydroxyphenylacetic acid*, $\text{OH}\cdot\text{C}_6\text{Br}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, prepared from the nitrile, crystallises in needles melting and decomposing at 265° ; its *acetyl* derivative forms crystals melting at $250-255^{\circ}$; its *methyl ester* crystallises in needles melting at $220-221^{\circ}$, and forms a

sparingly soluble *sodium* derivative and an *acetyl* derivative which crystallises in needles melting at 159°. The *amide*,



formed as an intermediate product in the preparation of the acid, crystallises in prisms.

Tetrabromo-p-hydroxybenzyl nitrite, $\text{OH}\cdot\text{C}_6\text{Br}_4\cdot\text{CH}_2\cdot\text{ONO}$, prepared from the tetrabromo- ψ -bromide and potassium nitrite, crystallises in needles from benzene melting and decomposing at 143°, and when boiled with a methyl-alcoholic solution of sodium hydroxide is converted into tetrabromo-*p*-hydroxybenzyl methyl ether. Its *acetyl* derivative crystallises in leaflets melting at 172–173°.

Tetrabromo-p-hydroxybenzyl mercaptan, $\text{OH}\cdot\text{C}_6\text{Br}_4\cdot\text{CH}_2\cdot\text{SH}$, prepared by treating the ψ -bromide with alcoholic solution of sodium hydrogen sulphide, crystallises in prisms or needles melting at 152°, and is reconverted into the ψ -bromide by heating with bromine. Its *diacetyl* derivative forms crystals melting at 132–133°. *Tetrabromo-p-hydroxybenzyl sulphide*, $(\text{OH}\cdot\text{C}_6\text{Br}_4\cdot\text{CH}_2)_2\text{S}$, is formed at the same time as the mercaptan, and is a crystalline powder decomposing at 255°.

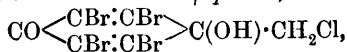
The *oxide*, $\text{CO}\begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}:\text{CBr} \end{smallmatrix}\text{C}\begin{smallmatrix} \text{O} \\ \text{CH}_2 \end{smallmatrix}$, is obtained from pentabromo-tolu- ψ -quinol (*loc. cit.*) by regulated treatment of its alcoholic solution with aqueous sodium carbonate; aniline converts the tolu- ψ -quinol into the compound $\text{CO}\begin{smallmatrix} \text{CBr}:\text{C}(\text{NHPh}) \\ \text{CBr}=\text{CBr} \end{smallmatrix}\text{C}\begin{smallmatrix} \text{O} \\ \text{CH}_2 \end{smallmatrix}$, which crystallises in yellow leaflets melting and decomposing at 209°. When the oxide is heated with a saturated solution of hydrogen bromide in acetic acid, it yields the compound $\text{OH}\cdot\text{C}\begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}:\text{CBr} \end{smallmatrix}\text{C}\cdot\text{O}\cdot\text{CH}_2\text{Br}$, which crystallises in white needles melting at 150–160°; its *acetyl* derivative, prepared either directly from the compound or by treating the oxide with acetyl bromide and a little concentrated sulphuric acid, crystallises in leaflets melting at 144–145°. When heated with sulphuric acid in acetic acid solution, tetrabromoquinone and tetrabromoquinol are formed.

Tetrabromomethylenequinone, $\text{CO}\begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}:\text{CBr} \end{smallmatrix}\text{C}:\text{CH}_2$ (or a polymeride), is obtained by eliminating hydrogen bromide from the tetrabromo-*p*-cresol ψ -bromide by shaking its benzene solution with anhydrous sodium acetate, and is an amorphous, white powder, which is oxidised to tetrabromobenzoquinone by nitric acid, and is reconverted into the ψ -bromide by hydrogen bromide; by alkalis in acetone solution, it is changed to tetrabromo-*p*-hydroxybenzyl alcohol and tetrabromo-*p*-hydroxybenzylacetone. It yields tetrabromo-*p*-hydroxybenzyl methyl ether with methyl alcohol, and with acetic anhydride, tetrabromo-*p*-acetoxybenzyl acetate. With aniline, it yields two *anilides*, one identical with that obtained by the action of aniline on the ψ -bromide, and a *second*, probably $\text{CO}\begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}:\text{CBr} \end{smallmatrix}\text{CH}\cdot\text{CH}_2\cdot\text{NHPh}$, which crystallises in yellow needles melting at 203–205°.

Tetrabromo-p-cresol ψ -chloride, $\text{C}_7\text{H}_5\text{OClBr}_4$, prepared from tetra-

bromo-*p*-hydroxybenzyl alcohol and hydrogen chloride, crystallises in needles melting at 174° and resembles the ψ -bromide; its *acetyl* derivative crystallises in needles melting at 180—181°, and when boiled with acetic anhydride is converted into tetrabromo-*p*-acetoxybenzyl acetate. An *isomeride* of the acetyl derivative is obtained when the ψ -chloride is boiled with sodium acetate and acetic acid; it melts at 159—160°.

ω -Chloro-2 : 3 : 5 : 6-tetrabromotolu- ψ -quinol,



prepared by heating the ψ -chloride with nitric acid, crystallises in yellow needles melting at 175—176°; its *acetyl* derivative crystallises in needles melting at 154—155°; both are converted into the oxide above described by treatment with alkalis. Aniline converts the

tolu- ψ -quinol into an *anilide*, $\text{CO} \begin{array}{c} \text{CBr}:\text{C}(\text{NHPh}) \\ \text{CBr}=\text{CBr} \end{array} \text{C}(\text{OH})\cdot\text{CH}_2\text{Cl}$ or $\text{CO} \begin{array}{c} \text{C}(\text{NHPh}):\text{CBr} \\ \text{CBr}=\text{CBr} \end{array} \text{C}(\text{OH})\cdot\text{CH}_2\text{Cl}$, which crystallises in yellowish-red needles melting at 180—181°.

K. J. P. O.

Derivatives of the Volatile Nitroresorcinol. HUGO KAUFFMANN and ERWIN DE PAY (*Ber.*, 1906, 39, 323—328. Compare *Abstr.*, 1904, i, 157).—The *hydrochloride* of 2-aminoresorcinol, $\text{C}_6\text{H}_7\text{O}_2\text{N}\cdot\text{HCl}$, is prepared by reducing 2-nitroresorcinol with tin and hydrochloric acid at 85°, saturating the cooled reaction-product with hydrogen chloride, and recrystallising the precipitate from concentrated hydrochloric acid; it is obtained in white, well-formed crystals. The free *base* is unstable and cannot be isolated; it reduces ammoniacal silver and Fehling's solutions, and may be used as a photographic developer. The action of sodium nitrite on the cooled solution of the hydrochloride leads to the formation of a *nitroso*-derivative of resorcinol diazonium anhydride, $\text{C}_6\text{H}_3\text{O}_3\text{N}_3$, which crystallises from acetone in greyish-green needles, begins to decompose at 176°, and explodes at 195°; it dissolves in aqueous alkali hydroxides to form red solutions, from which it is reprecipitated unchanged on acidification.

Dibenzoyl-2-nitroresorcinol, formed from 2-nitroresorcinol by the action of benzoyl chloride and sodium carbonate, crystallises from alcohol in yellowish-white needles and melts at 140° (compare Pechmann and Obermiller, *Abstr.*, 1901, i, 336). When reduced with iron powder and glacial acetic acid, it yields 2-benzoylaminoresorcinol, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{NHBz}$, which crystallises from alcohol in nacreous leaflets, melts at 187°, and is soluble in aqueous alkali hydroxides, and 3-benzoxyl-1-phenylbenzoxazole, $\text{OBz}\cdot\text{C}_6\text{H}_3 \begin{array}{c} \text{O} \\ \text{N} \end{array} \text{CPh}$, which crystallises from light petroleum in white leaflets, melts at 140°, and is insoluble in aqueous alkali hydroxides.

When treated with sodium nitrite and dilute hydrochloric acid, 2-benzoylaminoresorcinol yields a *nitroso*-derivative, $\text{C}_{13}\text{H}_{10}\text{O}_4\text{N}_2$, which crystallises in red needles, melts at 208°, and dissolves without decomposing in aqueous alkali hydroxides.

2-Nitroresorcinol couples with 1 mol. of benzenediazonium chloride in alkaline solution to form the *mono-azo-dye*, $C_{12}H_9O_4N_3$, which crystallises from glacial acetic acid in dark red needles, melts at 171° , and is soluble in aqueous alkali hydroxides, forming orange-red solutions.

The *azo-dye*, $C_{18}H_{13}O_4N_5$, formed by coupling 2-nitroresorcinol with 2 mols. of benzenediazonium chloride, crystallises in dark red needles and commences to decompose at 260° ; it dissolves in dilute alkali hydroxides to form violet-red solutions.

The nitro-azo-dyes were compared spectroscopically with the corresponding resorcinol dyes in sulphuric acid and in acetone solution containing $4/3 \times 10^{-3}$ mol. per litre. All the solutions exhibit absorption at the violet end of the spectrum only; with the nitro-dyes, in long layers (20 cm.), the absorption extends further into the yellow than with the resorcinol derivatives; the difference is greatest with the mono-azo-dyes in acetone solution. The introduction of a nitro-group into a resorcinol azo-dye is accompanied by a slight increase in the depth of colour.

2-Nitroresorcinol interacts with benzenediazonium chloride in acid-alcoholic solution to form a *substance*, $C_{12}H_9O_4N_3$, which crystallises from glacial acetic acid in light red needles and melts at $175-176^\circ$.

G. Y.

Action of Hydroxylamine on Dimethyldihydroresorcin.

W. GITTEL (*Chem. Centr.*, 1906, i, 33—35; from *Zeit. für Naturwiss.*, 77, 145—173).—Dimethyldihydroresorcin yields a crystalline and an amorphous oxime, both of which have the same molecular weight. Since the amorphous form, which is stable in the presence of acids, cannot be converted into a dioxime, it would appear to have the constitution of a hydroxamic acid, $CM_e_2 \begin{array}{c} \text{CH}_2 \text{---} \text{CO} \\ \text{CH}_2 \cdot C(NH \cdot OH) \end{array} > CH$.

On the other hand, however, the fact that both forms have faintly acid properties renders it more probable that they are stereoisomerides. The anilino-derivative of dimethyldihydroresorcin only exists in one form, which resembles that of the amorphous oxime; it neither yields a dianilino-derivative nor a dioxime.

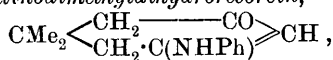
The amorphous *oxime*, $CM_e_2 \begin{array}{c} \text{CH}_2 \text{---} \text{CO} \\ \text{CH}_2 \cdot C(N \cdot OH) \end{array} > CH_2$, prepared by the action of hydroxylamine hydrochloride on dimethyldihydroresorcin, separates from ether in the form of a brittle mass which is soluble in alcohol, chloroform or benzene, somewhat soluble in a large quantity of a solution of sodium carbonate, and very readily so in potassium hydroxide, acetic acid, or dilute hydrochloric acid; it gives a reddish-brown coloration with ferric chloride and reduces Fehling's solution on warming. It neither forms an oxime nor yields crystalline compounds with acetic anhydride in presence of hydrogen chloride or concentrated sulphuric acid. The *hydrochloride* of the crystalline *oxime*, $C_{18}H_{14}O_2NCl$, obtained by allowing the oxime to remain with concentrated hydrochloric acid for six days, forms large crystals, melts about 152° , and is readily soluble in alcohol or water, but insoluble in

ether. It is not readily attacked by concentrated hydrochloric acid; its aqueous solution gives a yellow precipitate with formaldehyde which melts at 78—80°.

The crystalline *oxime* forms a white mass which melts at 115° and is soluble in hot water, alkali hydroxides, hydrochloric acid, or acetic acid; it reduces alkaline solutions of copper or ammoniacal solutions of silver on warming, and gives a reddish-brown coloration with ferric chloride, but is not attacked by warm acetic anhydride. By the action of semicarbazide in alkaline solution, an amorphous, brick-red substance is formed which is soluble in hydrochloric acid and potassium hydroxide, forming yellow and red solutions respectively.

The *dioxime*, $\text{CMe}_2 \left\langle \begin{array}{c} \text{CH}_2 \cdot \text{C}(\text{N} \cdot \text{OH}) \\ \text{CH}_2 \cdot \text{C}(\text{N} \cdot \text{OH}) \end{array} \right\rangle \text{CH}_2$ (compare Vorländer, Abstr., 1897, i, 273), prepared from the crystalline oxime or from dimethyldihydroresorcin, is soluble in alkali hydroxides, hydrochloric acid, or acetic acid, but is insoluble in a solution of sodium carbonate; it reduces an alkaline solution of copper, and with ferric chloride gives a faint brown coloration which gradually becomes darker. Benzoyl chloride and acetic anhydride yield amorphous products. The *ethyl* derivative, prepared by the action of ethyl iodide and sodium on the dioxime, separates as a resin which is soluble in hydrochloric or acetic acid, less so in solutions of alkali hydroxides, and insoluble in sodium carbonate. The *hydrochloride*, $\text{C}_8\text{H}_{15}\text{O}_2\text{N}_2\text{Cl}$, forms highly refractive, colourless crystals, which are probably monoclinic and are readily soluble in alcohol; it becomes darker at 175° and decomposes at 185° without melting. The *phenylhydrazone*, $\text{CMe}_2 \left\langle \begin{array}{c} \text{CH}_2 - \text{CO} \\ \text{CH}_2 \cdot \text{C}(\text{N}_2\text{HPh}) \end{array} \right\rangle \text{CH}_2$, is a hygroscopic, bright yellow powder, which on exposure to air becomes flesh-coloured to orange-red and melts and decomposes at 158°. It is soluble in alcohol or acetone, sparingly so in chloroform, and insoluble in ethyl acetate, ether, carbon disulphide, light petroleum, benzene, hydrochloric acid, or potassium hydroxide and gives a slight brown coloration with ferric chloride. The alcoholic solution forms a deep blue coloration with dilute nitric acid and becomes green when warmed with dilute sulphuric acid. When concentrated hydrochloric acid is poured over the phenylhydrazone, a white substance is obtained which becomes dark at 170° and melts at 181°. When treated with dry hydrogen chloride, the phenylhydrazone becomes emerald-green, but by the action of the gas on the powder suspended in chloroform or ethyl acetate, the liquid changes to bluish-green, bright blue, and finally to greyish-blue or violet, and a *compound*, $\text{C}_{23}\text{H}_{13}\text{N}_5\text{Cl}$ (?), is formed, the phenylhydrazone being partially decomposed and dimethyldihydroresorcin regenerated; the compound forms a white powder which, on exposure to the atmosphere, partially becomes blue. By the action of concentrated alkaline solutions, orange-red flakes are formed, which rapidly become scarlet and dissolve in alcohol, forming an orange-red solution. When the solution is treated with hydrochloric acid, it becomes green, then blue, and finally olive-green, and an amorphous, flocculent precipitate is formed; ammonia restores the orange-red

colour of the solution. By the action of dilute nitric acid, a blackish-brown dye is formed, and when treated with a small quantity of concentrated sulphuric acid a product is obtained which is possibly a sulphonic acid. *Anilinodimethyldihydroresorcin*,



separates from its alcoholic solution in white crystals, melts at 181° , is readily soluble in alcohol, chloroform, or glacial acetic acid, less so in hydrochloric acid, sparingly soluble in acetone, ether, or light petroleum, and insoluble in potassium hydroxide; it gives a wine-red coloration with ferric chloride and a blackish-brown dye is formed by the action of nitrous acid.

The *hydrochloride*, $\text{C}_{14}\text{H}_{18}\text{ONCl}$, prepared by passing hydrogen chloride into a solution of the anilino-derivative in chloroform, is a white substance which crystallises from alcohol, sinters at 205° , and melts at $214\text{--}217^\circ$. The *acetoxy*-derivative separates from ethyl acetate in the form of a yellow, crystalline mass which sinters at 57° and melts at 62° ; it is readily soluble in alcohol, ether, chloroform, or light petroleum, less so in hydrochloric acid in presence of alcohol, and only sparingly so in potassium hydroxide. It does not give a reaction with ferric chloride, but is decomposed by concentrated hydrochloric acid at the ordinary temperature.

The *o-toluidino*-derivative, $\text{C}_{15}\text{H}_{19}\text{ON}$, crystallises from aqueous alcohol in slender needles, melts at 135° , and gives a reddish-brown coloration with ferric chloride. The *hydrochloride*, $\text{C}_{15}\text{H}_{20}\text{ONCl}$, separates from the alcoholic solution in white crystals, sinters at 204° , and melts at 208° ; when treated with water, it becomes yellow and is apparently decomposed. The *p-toluidino*-derivative crystallises from alcohol and melts at 202° ; the *hydrochloride* forms strongly etched crystals, is soluble in alcohol, sinters at 197° , and becomes dark and melts at $206\text{--}210^\circ$. The *α -naphthylamino*-derivative separates from the alcoholic solution in a greyish-white, crystalline form, melts at 175° , and gives a blood-red coloration with ferric chloride; the *hydrochloride* forms rectangular crystals, melts at $226\text{--}230^\circ$, is soluble in alcohol or chloroform, insoluble in ether, and gives a reddish-brown coloration with ferric chloride.

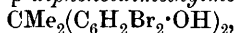
It is probable that phenyldihydroresorcin also forms two isomeric oximes. The greasy, yellow substance which is obtained together with a resinous product by the action of hydroxylamine hydrochloride on phenyldihydroresorcin melts at $95\text{--}103^\circ$, is soluble in alcohol (compare Vorländer, *loc. cit.*), and reduces Fehling's solution on warming; its solution in hydrochloric acid is yellow and in alkali red. The main product of the reaction, however, forms a white, resinous mass which, on exposure to the atmosphere, becomes successively yellow, orange, and brown. With glacial acetic acid, it yields a small quantity of a substance which melts at $185\text{--}187^\circ$ and is readily soluble in potassium hydroxide, but only sparingly so in hydrochloric acid or a solution of sodium carbonate; by the action of acetic anhydride and dry hydrogen chloride, a portion probably is converted into the crystalline oxime which melts at $79\text{--}82^\circ$.

E. W. W.

Action of Bromine and Chlorine on Phenols. Substitution Products. ψ -Bromides and ψ -Chlorides. XIV. Action of Bromine on *p*-Diphenoldimethylmethane. ψ -Bromides and Quinones of *p*-isoPropylphenol. THEODOR ZINCKE and MAX GRÜTERS (*Annalen*, 1905, 343, 75—99. Compare Abstr., 1904, i, 41, 401, 1005; 1905, i, 55, 342).—The ψ -bromide of isopropylphenol is obtained from diphenoldimethylmethane, which readily decomposes into phenol and isopropylphenol.

p-Diphenoldimethylmethane, $\text{CMe}_2(\text{C}_6\text{H}_4\cdot\text{OH})_2$, is prepared by warming a mixture of phenol, acetone, and concentrated hydrochloric acid for three days and then treating the mixture with 40 per cent. acetic acid; it crystallises in colourless needles or prisms melting at $152\text{--}153^\circ$.

3 : 5 : 3' : 5'-Tetrabromo-*p*-diphenoldimethylmethane,



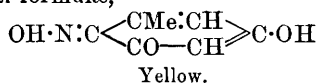
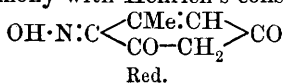
prepared by the action of bromine in acetic acid on the compound last mentioned, crystallises in prisms or spikes melting at $162\text{--}163^\circ$ and is soluble in alkali hydroxides without decomposition; the *acetyl* derivative crystallises in needles melting at $169\text{--}170^\circ$. When a solution of the tetrabromide in acetic acid is treated with solid sodium nitrite at the ordinary temperature, two atoms of bromine are replaced by nitro-groups, a 3 : 3'-dibromo-5 : 5'-dinitro-*p*-diphenoldimethylmethane, $\text{C}_{15}\text{H}_{12}\text{O}_6\text{N}_2\text{Br}_2$, being formed; it crystallises in yellow needles melting at 176° , and yields red ammonium and alkali salts; its *acetyl* derivative crystallises in yellow needles melting at $196\text{--}197^\circ$.

ψ -*p*-Tribromoisopropyltetrabromophenol (ψ -heptabromo-*p*-isopropylphenol), $\text{CO} \begin{smallmatrix} \text{CBr}\cdot\text{CBr} \\ \text{CBr}\cdot\text{CBr} \end{smallmatrix} \text{CH}\cdot\text{CBrMe}\cdot\text{CHBr}_2$, is formed together with tribromophenol when the tetrabromide described above is heated with bromine at 100° ; it crystallises in prisms melting and decomposing at $182\text{--}183^\circ$, and when treated with acetone is immediately converted into hexabromoquinone; with acetic anhydride at the ordinary temperature, a heptabromoacetyl derivative is produced, and at a higher temperature the pentabromoacetyl derivative. *Acetylheptabromo-p*-isopropylphenol, $\text{C}_{11}\text{H}_7\text{O}_2\text{Br}_7$, crystallises in colourless needles melting at 166° , and by alcoholic potash is converted into hexabromoisopropenylphenol.

p-Dibromoisopropylidenetetrabromoquinone (hexabromoisopropylidenequinone), $\text{CO} \begin{smallmatrix} \text{C} \text{ 3r} \cdot \text{CBr} \\ \text{C} \text{ 3r} \cdot \text{CBr} \end{smallmatrix} \text{C} \cdot \text{CMe} \cdot \text{CHBr}_2$, is prepared by slowly adding water to an acetone solution of the heptabromide, and crystallises in yellow needles or prisms melting at 185° . When treated with acetic anhydride in the presence of sulphuric acid at the ordinary temperature, it is converted into *p*- α -dibromo- β -acetoxyisopropyltetrabromophenyl acetate, $\text{OAc}\cdot\text{C}_6\text{Br}_4\cdot\text{CMe}(\text{OAc})\cdot\text{CHBr}_2$, which crystallises in prisms melting at $144\text{--}145^\circ$; when hydrolysed, it yields not the corresponding phenol but hexabromoisopropenylphenol. The corresponding *phenolalcohol* is formed in small quantity when the quinone is treated with sulphuric acid in acetic acid solution, and crystallises in needles melting at $114\text{--}117^\circ$. It readily loses water, forming the

propenyl derivative. *p*-Dibromoisopropenyltetra-bromophenol (*hexabromo-p-isopropylenephenol*), $\text{OH}\cdot\text{C}_6\text{Br}_4\cdot\text{CMe}\cdot\text{CBr}_2$, formed by hydrolysing the heptabromo-acetate in alcoholic solution or by reduction of the quinone with an alkaline solution of stannous chloride, crystallises in colourless needles melting at $134-135^\circ$; it yields a sparingly soluble *sodium* salt, and is again converted into the ψ -heptabromide by hydrobromic acid in acetic acid solution. The *acetyl* derivative crystallises in monoclinic prisms melting at $114-115^\circ$. *p*-Bromoisopropenyltetra-bromophenol (*pentabromo-p-isopropylenephenol*), $\text{OH}\cdot\text{C}_6\text{Br}_4\cdot\text{CMe}\cdot\text{CHBr}$, prepared from the hexabromoisopropylidenequinone by keeping its acetone solution or by reducing the hexabromoquinone with stannous chloride in acetic acid solution, crystallises in needles melting at $88-89^\circ$; it yields a crystalline *sodium* salt, is converted by bromine into the heptabromo- ψ -bromide, and with nitric acid yields a crystalline product. Its *acetyl* derivative crystallises in monoclinic prisms melting at $126-127^\circ$, and is formed when the heptabromo- ψ -bromide or hexabromoquinone is boiled with acetic anhydride. K. J. P. O.

The Isomeric Nitroso-orcinols. ARTHUR HANTZSCH and C. H. SLUITER (*Ber.*, 1906, 39, 162—166. Compare Henrich, *Abstr.*, 1900, i, 163, 436; 1901, i, 464; Hantzsch and Voegelen, 1902, i, 260).—Henrich's yellow modification of nitroso-orcinol crystallises from alcohol in yellowish-brown needles, decomposes at 163° , and has $K=0\cdot037$. Its aqueous solution has an orange-yellow colour. The red modification crystallises from boiling benzene and has a transition temperature $124-125^\circ$ and $K=0\cdot051$. Its aqueous solutions are orange-red in colour, and are perfectly stable when the compounds are pure, otherwise there is a tendency to the formation of an equilibrium mixture of the two; the point of equilibrium is not reached, however, even at the end of several weeks. The addition of alcohol immediately causes the equilibrium to be attained, solutions of both substances then have the same conductivity. Raising the temperature to 50° does not produce the change of the one form into the other. Both modifications yield the same potassium or ammonium salt. These facts are in harmony with Henrich's constitutional formulæ,



J. J. S.

Replacement of the Acetyl Group by Methoxyl under the Action of Diazomethane. JOSEF HERZIG and J. TICHATSCHKE (*Ber.*, 1906, 39, 268).—When triacetylpyrogallol is exposed to the action of diazomethane at the ordinary temperature for forty-eight hours, the product is found to contain 10·4 per cent. of methoxyl. The acetyl derivative of phloroglucinol diethyl ether is under similar conditions converted almost completely into phloroglucinol methyl diethyl ether.

W. A. D.

Peculiar Behaviour of Hexabromodiresorcinol in Alkaline Solution. HEINRICH BECHHOLD (*Zeit. Elektrochem.*, 1905, 11, 845—846).—When dissolved in less than 2·5 molecules of alkali

hexabromodiresorcinol oxidises in presence of the atmosphere to a blue colouring matter, when more alkali is used the solution remains unchanged. The different ionisation in the two cases is suggested as the cause of the difference. T. E.

α - and β -Campholytic Alcohols. GUSTAVE BLANC (*Compt. rend.*, 1906, 142, 283—285. Compare Abstr., 1900, i, 581; 1905, i, 11).—*Dihydro- β -campholyl alcohol*, $C_8H_{15}\cdot CH_2\cdot OH$, obtained by reducing ethyl β -campholytate or the corresponding amide with alcohol and sodium is a colourless, viscous liquid which boils at 198° , has a sp. gr. 0.9056 at $21.5^\circ/4^\circ$, and n_D 1.4641 at 21.5° . The *pyruvate*, $C_8H_{15}\cdot CH_2\cdot O\cdot CO\cdot COMe$, is a mobile liquid boiling at 140 — 142° under 17 mm. pressure and has an agreeable penetrating odour; the *semicarbazone* crystallises from alcohol and melts at 158° ; the *chloride*, $C_8H_{15}\cdot CH_2Cl$, boils at 175° .

α -Campholyl alcohol, $\begin{matrix} CMe\cdot CMe_2 \\ | \\ CH-CH_2 \end{matrix} > CH\cdot CH_2\cdot OH$, obtained by reducing the ethyl ester or the amide of α -campholytic acid with alcohol and sodium, is a viscous liquid boiling at 200° and having a sp. gr. 0.9273 at $23^\circ/4^\circ$ and n_D 1.4762 at 23° ; the *pyruvate*, $C_8H_{13}\cdot CH_2\cdot O\cdot CO\cdot COMe$, boils at 143 — 144° under 17 mm. pressure; the *semicarbazone* melts at 137° . M. A. W.

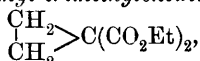
Cholesterol. V. ADOLF WINDAUS (*Ber.*, 1906, 39, 518—523. Compare Abstr., 1904, i, 49, 667, 1010; 1905, i, 128; Diels and Abderhalden, Abstr., 1904, i, 880).—Chromic acid and acetic acid at 70° , or sulphuric acid and potassium permanganate in the cold, oxidise dibromocholesterol to dibromocholestenone, which is reduced to cholestenone by zinc dust and acetic acid. Cholestenone gives a rose-red coloration with concentrated nitric acid; when heated on the water-bath with a mixture of equal volumes of acetic acid and nitric acid of sp. gr. 1.4, it yields a *nitro-derivative*, probably $C_{27}H_{41}O_6N_3$, which crystallises from acetone in glassy leaflets melting at 194 — 195° . Cholestenone is stable towards a 3 per cent. alcoholic solution of hydrogen chloride, a 10 per cent. alcoholic solution of potassium hydroxide, or towards diethylamine; when heated at 210 — 220° with piperidine, it yields a *substance*, $C_{32}H_{51}N$ or $C_{32}H_{53}N$, which forms large crystals melting at 159° .

Cholestenone is probably not an $\alpha\beta$ -unsaturated ketone, since its reduction by sodium amalgam in 95 per cent. alcoholic solution gives an unsaturated *pinacone*, $C_{54}H_{80}O_2$ or $C_{54}H_{90}O_2$, crystallising in needles which sinter and melt at 221° (compare Harries, Abstr., 1904, i, 427). With acetic anhydride, the pinacone yields a *hydrocarbon*, $C_{54}H_{82}$ or $C_{54}H_{86}$ (compare Lieben, Abstr., 1905, i, 167). The same hydrocarbon seems to be produced by the reduction of cholestenone with zinc dust and alcoholic hydrogen chloride, and in the reduction of dibromocholestenone. C. S.

Ergosterol. D. OTTOLENGHI (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 697—705. See this vol., ii, 202).

Action of Ethylene Dibromide on Ethyl Sodiocyanoacetate. LÉONCE BARTHE (*Bull. Soc. chim.*, 1906, [iii], 35, 40—47. Compare Abstr., 1894, i, 492).—The author has repeated the work of Carpenter and Perkin (*Trans.*, 1899, 75, 924) and generally confirmed their observations.

Ethyl cyanotrimethylenecarboxylate, $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > \text{C}(\text{CN}) \cdot \text{CO}_2\text{Et}$, boils at 137° under 80 mm. pressure and is hydrolysed by hydrogen chloride in presence of alcohol to *ethyl trimethylenedicarboxylate*,



which is a colourless, oily liquid and boils at 130° under 70 mm. pressure. The author cannot confirm Carpenter and Perkin's statement that ethyl cyanotrimethylenecarboxylate is hydrolysed by potassium hydroxide in alcohol to the corresponding cyano-acid, but a small yield of the latter was obtained by adding metallic sodium to a solution of the ester in alcohol. The *magnesium* salt crystallises with H_2O .

The crystalline accessory substance melting at 119° obtained by Carpenter and Perkin (*loc. cit.*), and which, since it yielded adipic acid on hydrolysis, they regarded as ethyl *ad-dicyanovale*rate, furnished malonic acid when hydrolysed with hydrochloric acid. Hydrolysis carried out with other agents gave the present author inconclusive results.

T. A. H.

Terpenes and Ethereal Oils. LXXIV. *cyclo*Hexanone. OTTO WALLACH (*Annalen*, 1905, 343, 40—53).—This paper contains in part an account of work previously published, together with corrections and amplifications.

*cyclo*Hexanoneisooxime, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \end{array} > \text{NH}$, yields on hydrolysis ϵ -aminohexoic acid, $\text{NH}_2 \cdot \text{CH}_2 \cdot [\text{CH}_2]_4 \cdot \text{CO}_2\text{H}$, which is oxidised by alkaline permanganate to normal adipic acid. Suberoneisooxime similarly yields ζ -aminoheptoic acid, which is oxidised to pimelic acid.

On reducing the hexanoneisooxime with sodium in amyl alcohol solution, unsaturated fatty acids are mainly formed together with *cyclohexylamine* (not, as was expected, hexamethyleneimine, Abstr., 1905, i, 826), $\text{C}_6\text{H}_{11} \cdot \text{NH}_2$, which is an oil boiling at 135—138° and having a sp. gr. 0.863 and n_D 1.4575 at 24°. The *hydrochloride* melts at 203—204°, the *benzoyl* derivative at 149°, the *carbamide* at 195—196°, and the *methiodide* at 260°. The amine is probably formed from the hexamethyleneimine by fission into an intermediary acyclic compound, which by renewed ring formation passes into *cyclohexylamine*. Some hexamethyleneimine seems to be present in the more volatile fractions.

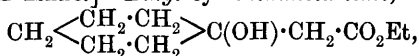
When ϵ -aminohexoic acid is oxidised with nitric acid, ϵ -hydroxyhexoic acid is formed. The latter loses water, forming a mixture of Δ^6 - and Δ^7 -hexenoic acids.

Tetrahydrobenzene forms a nitrosochloride when a solution of the

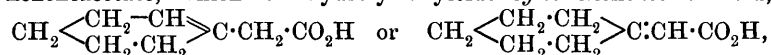
hydrocarbon in acetic acid is treated successively with ethyl nitrite and concentrated hydrochloric acid. The nitrosochloride is an unusually stable substance.

1-Methylcyclohexane-2-one is prepared from Δ^1 -tetrahydrotoluene which can now be easily obtained by Grignard's method from methyl iodide and cyclohexanone; this reaction first yields 1-methylcyclohexane-1-ol. The latter is then dehydrated.

[With EDUARD ISAAC.]—Ethyl cyclohexanolacetate,



is prepared from cyclohexanone and ethyl bromoacetate by the agency of magnesium. It passes readily by loss of water into ethyl cyclohexeneacetate, which on hydrolysis yields cyclohexeneacetic acid,



melting at 37–38° and boiling at 140° under 12 mm. pressure. It takes up bromine in ethereal solution, giving dibromocyclohexaneacetic acid, $\text{C}_6\text{H}_{12}\text{O}_2\text{Br}_2$, which crystallises in prisms melting at 119–120° and is converted into an oil on treatment with alkali carbonates.

When cyclohexeneacetic acid is oxidised at 0° by permanganate, a cyclohexanone is not formed, but a compound with seven carbon atoms which is not an aldehyde.

K. J. P. O.

5-Bromo-2-aminobenzoic Acid and Certain Derivatives.

MARSTON T. BOGERT and WILLIAM F. HAND (*J. Amer. Chem. Soc.*, 1905, 27, 1476–1484).—5-Bromo-2-acetylaminobenzoic acid (5-bromo-acetylanthranilic acid) (Jackson, Abstr., 1881, 735) was prepared by the direct bromination of acetylanthranilic acid, by the oxidation of 5-bromo-*o*-acetyltoluidine, and by the hydrolysis of 5-bromoacetylanthranil; it crystallises in transparent, six-sided, microscopic prisms and melts at 222–223° (corr.). The barium salt was prepared. 5-Bromo-2-aminobenzoic acid melts at 219–220° (corr.), and not at 211.5–212° as stated by Alt (Abstr., 1889, 987); its hydrochloride and barium salt are described. 5-Bromoacetylanthranil crystallises in colourless scales and melts at 131° (corr.). 5-Bromo-2-acetylaminobenzonitrile, obtained by the action of bromine on acetylaminobenzonitrile, forms six-sided prisms, melts at 158° (corr.), and is easily soluble in alcohol, acetone, ethyl acetate, hot benzene, or chloroform, and sparingly so in water.

E. G.

Stereoisomeric Cinnamic Acids. EMIL ERLÉNMEYER, jun.

(*Ber.*, 1906, 39, 285–292. Compare Abstr., 1905, i, 892; this vol., i, 21).—Synthetically prepared cinnamic acid gives with brucine in alcoholic solution three different brucine salts of the same composition, melting at 135°, 113°, and 107° respectively. Cinnamic acid from storax gives only the brucine salt melting at 135°, which in 1 per cent. alcoholic solution is optically inactive. The salt melting at 113° in 1 per cent. alcoholic solution has $[\alpha]_D - 12.5^\circ$. Cinnamic acid from storax has a solubility in absolute alcohol of 12.72 grams per 100 c.c., whilst synthetical cinnamic acid has a somewhat greater solubility, namely, 13.88 grams per 100 c.c.; the two acids show a strikingly

different behaviour when recrystallised from alcohol. Cinnamic acid from storax is converted into synthetical cinnamic acid when heated for ten hours with concentrated sodium hydroxide. All three of the brucine salts separated from alcohol give, on crystallisation from benzene, the same product, $C_9H_8O_2 \cdot C_{23}H_{26}O_4Na \cdot C_6H_6$, melting at $92-93^\circ$; but on volatilising the benzene of crystallisation at $70-80^\circ$, the differences between the salts reappear.

On combining synthetical cinnamic acid with *l*-isodiphenyloxyethylamine and crystallising from alcohol, two different *salts* containing alcohol of crystallisation are obtained; the more soluble *salt* melts, when the alcohol has been expelled, at 128° , and in 1 per cent. alcoholic solution gives $[\alpha]_D - 46.5^\circ$; the less soluble *salt* melts at $136-137^\circ$ and has $[\alpha]_D - 63.5^\circ$. From *d*-isodiphenyloxyethylamine and synthetical cinnamic acid, two analogous *salts* are obtained, melting at 136° and 128° with nearly corresponding dextro-rotations.

With storax cinnamic acid, *l*-isodiphenyloxyethylamine gives only a *salt* containing 2EtOH, which, when dried in the air, melts at $75-80^\circ$, and when dried at 80° melts at 128° ; in 1 per cent. alcoholic solution it has $[\alpha]_D - 44.4^\circ$. With the same acid, *d*-isodiphenyloxyethylamine gives a *salt* melting at $130-132^\circ$ when dried in the air, and at 136° when dried at 80° ; in 1 per cent. alcoholic solution, it has $[\alpha]_D + 64^\circ$.

Storax cinnamic acid thus seems to be a component of synthetical cinnamic acid. The cases which the author has dealt with seem to point to the existence of a new class of stereoisomerism; its nature is briefly discussed.

W. A. D.

Action of Pyridine on Salicyl Chlorides. RICHARD B. EARLE and H. LOUIS JACKSON (*J. Amer. Chem. Soc.*, 1906, **28**, 104—114).—When pyridine is added to a solution of 3:5-dichlorosalicyl chloride, *dichlorosalicylide*, $(C_7H_2O_2Cl_2)_4$, corresponding with the salicylide described by Anschütz (Abstr., 1893, i, 165), is produced, which is insoluble in the usual solvents but is soluble in hot anisole or hot nitrobenzene, separates from the latter solvent in short, prismatic crystals, melts and decomposes at about 330° , and is very stable; it is very slowly attacked by aqueous potassium hydroxide, but is readily hydrolysed by alcoholic potassium hydroxide. The molecular weight was determined in boiling anisole; the constant *K* for this solvent was found to be 4502 (calculated, *K* = 4595).

3:5-Dibromosalicyl chloride, obtained by the action of phosphorus pentachloride on 3:5-dibromosalicylic acid, crystallises from light petroleum and melts at $83-85^\circ$. When pyridine is added to a solution of the chloride in light petroleum, cooled to -6° , a precipitate is produced which is probably a mixture of substances. On adding pyridine to a solution of the chloride in acetone, cooled to -16° , a precipitate is obtained which has no definite melting point and is easily soluble in chloroform or benzene; a cryoscopic determination of the molecular weight in benzene solution indicated that the substance was a *heptasalicylide*, but it is possible that its complexity changes on solution. The lack of a definite melting point suggested that changes take place in the molecular weight of the substance, and its behaviour on heating was therefore studied by means of a dilatometer; it was

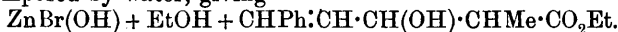
found that the substance behaves normally from 75° to 110°, contracts slowly at a constant rate from 110° to 170°, and expands at a rapidly increasing rate from 170° to 200°.

It was observed that during the action of pyridine on each chloride the solution at first became bright yellow, but rapidly faded, the duration of the colour varying with different solvents; a table is given recording the number of seconds during which the colour lasted in various solvents. The colour remained longest in a xylene solution, lasting in this case for about a minute.

On adding organic bases to the coloured solution, colourless precipitates are produced which are at present under investigation.

E. G.

Action of Zinc on a Mixture of Cinnamaldehyde and Ethyl α -Bromopropionate. L. BAIDAKOWSKY (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 896—902).—The action of a freshly-prepared zinc-copper couple on a mixture of cinnamaldehyde and ethyl α -bromopropionate in an atmosphere of carbon dioxide proceeds according to the equations: (1) $\text{CHMeBr} \cdot \text{CO}_2\text{Et} + \text{Zn} = \text{BrZn} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$; (2) $\text{CHPh} \cdot \text{CH} \cdot \text{CHO} + \text{BrZn} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et} = \text{CHPh} \cdot \text{CH} \cdot \text{CH}(\text{OZnBr}) \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$, which is decomposed by water, giving

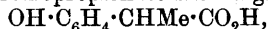


This ester could not be distilled unchanged, and on hydrolysis with 10 per cent. potassium hydroxide or sulphuric acid solution it yields cinnamenylcrotonic acid, $\text{CHPh} \cdot \text{CH} \cdot \text{CH} \cdot \text{CMe} \cdot \text{CO}_2\text{H}$. If, however, the ester is hydrolysed with cold 5 per cent. barium hydroxide solution, the *barium* salt, $\text{Ba}(\text{C}_{12}\text{H}_{13}\text{O}_3)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, is obtained as silvery leaflets and yields the *acid*, $\text{C}_{12}\text{H}_{14}\text{O}_3$, in a syrupy form; on boiling the latter with 10 per cent. sulphuric acid solution, it yields a lactone, cinnamenylcrotonic acid, and the unsaturated hydrocarbon, $\text{CHPh} \cdot \text{CH} \cdot \text{CH} \cdot \text{CHMe}$, isolated by Markownikoff (*Abstr.*, 1886, 1015) from Caucasian naphtha.

Cinnamenylcrotonic acid combines with bromine (4 atoms) giving a *compound* which melts and decomposes at about 130° and is readily soluble in alcohol, ether, or benzene, and slightly so in light petroleum.

T. H. P.

Action of Zinc on a Mixture of Salicylaldehyde and Ethyl α -Bromopropionate. Synthesis of α -Methylcoumarin. L. BAIDAKOWSKY (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 902—905).—The action of zinc or of a zinc-copper couple on a mixture of salicylaldehyde and ethyl α -bromopropionate should give the ester,



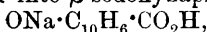
but the ester obtained could not be purified as it decomposed on distillation, giving salicylaldehyde and α -methylcoumarin.

T. H. P.

Preparation and Properties of β -Cumenyl- α -ethylhydracrylic Acid. A. KALISCHEFF (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 905—910).—The action of zinc on a mixture of cuminaldehyde and ethyl α -bromobutyrate yields ethyl β -cumenyl- α -ethylhydracrylate, which, on hydrolysis with sodium hydroxide and decomposition of the

sodium salt with dilute mineral acid, yields *β*-cumenyl-α-ethylhydracrylic acid, $C_3H_7 \cdot C_6H_4 \cdot CH(OH) \cdot CHEt \cdot CO_2H$, in two modifications, one soluble and the other insoluble in light petroleum. The latter separates from benzene or aqueous alcohol in small crystals melting at $124.5-125.5^\circ$; its *sodium*, *barium* ($4H_2O$), *calcium* ($4H_2O$), and *silver* salts were prepared and analysed. On distillation with dilute sulphuric acid, this acid loses water and carbon dioxide, yielding isopropyl-butenylbenzene, $C_3H_7 \cdot C_6H_4 \cdot CH:CHEt$.
T. H. P.

Carboxylation of Phenols by means of Carbon Dioxide.
II. *β*-Naphthol-1-carboxylic Acid. SIJBE TIJMSTRA, jun., and B. G. EGGINK (*Ber.*, 1906, **39**, 14—16. Compare Abstr., 1905, i, 439).—A modified method is described of preparing pure sodium *β*-naphthoxide. When heated with an excess of carbon dioxide at $110-120^\circ$, it is converted into *β*-sodoxynaphthoic acid,



which differs from sodium *β*-hydroxynaphthoate, $OH \cdot C_{10}H_6 \cdot CO_2Na$, in that it is capable of absorbing nearly one equivalent of dry ammonia.

2-Hydroxynaphthoic acid [*β*-naphthol-1-carboxylic acid] melts when quickly heated at 156° , liberating gas, and decomposes into naphthol and carbon dioxide when boiled with water; the acid contains a small quantity of water as represented by the formula $4C_{11}H_8O_3 \cdot H_2O$.

T. M. L.

Isomerism and Tautomerism. ARTHUR MICHAEL (*Ber.*, 1906, **39**, 203—211).—A discussion of the constitutions of ethyl formylphenylacetate, oxalacetic acid and its esters, and of dibenzoylacetyl-methane. When carbon dioxide is passed into a solution of the sodium derivative of ethyl formylphenylacetate, an oil is precipitated which quickly changes to a solid melting at about 50° . Using sulphuric acid of sp. gr. of at least 1.36 as the precipitant, a solid is at once obtained which melts at $98-100^\circ$. The use of a weaker solution of sulphuric acid causes the separation of an oil which changes somewhat slowly to a solid which melts between 60° and 90° and appears to be a mixture of the forms melting respectively at 50° and 100° . The modification melting at 50° is more soluble and is more easily transformed into the liquid tautomeride than is the form which melts at 100° .

The use of phenylcarbimide (Wislicenus, Abstr., 1896, i, 552) to differentiate between the enolic and ketonic forms is inadmissible, since all the modifications of ethyl formylphenylacetate unite with this reagent to form the ethereal carbanilide which melts at 116° . Normal tertiary fatty amines which unite only with enolic derivatives, are suitable reagents for the purpose in question, and, according to this criterion, all the forms of the ester are enolic.

[With ARTHUR MURPHY, jun.]—When a 10 per cent. solution of sulphuric acid is slowly added at 0° to a solution of the sodium derivative of methyl oxalacetate (Wislicenus and Grossman, Abstr., 1894, i, 116), a modification of the ester is obtained which melts at $85-87^\circ$ and is extraordinarily sensitive to heat, changing above 50°

into the ordinary form. Towards ferric chloride and other reagents, both modifications behave alike, and both are hydrolysed by hydrochloric acid into the oxalacetic acid which melts at 152° .

If to the mixture of the enolic and ketonic forms of dibenzoylacetylmethane, obtained by crystallising the ketonic form which melts at $107-110^{\circ}$ from 50 per cent. alcohol, a trace of acetic acid is added, and Claisen's directions are then followed (*Annalen*, 1896, **291**, 78), a new modification of the ketonic tautomeride is obtained, which melts at $147-149^{\circ}$; the same substance can be prepared in a similar way from the ketonic form melting at 110° or from the enolic form by the action of acetyl chloride. From ethylene dibromide, both the new and the old ketonic modifications of dibenzoylacetylmethane crystallise unchanged below 25° ; from methyl or ethyl alcohol, chloroform, or carbon tetrachloride, either form separates as a mixture of both modifications which melts at $126-136^{\circ}$, whilst the enolic tautomeride remains in solution. The new isomeride is at once enolised by benzene; so also is the old keto-derivative, contrary to Claisen's statement (*loc. cit.*). Of the two ketonic forms, the one with the higher melting point is the more stable and the less reactive. Triisobutylamine, in a solution of benzene and ether, converts the less fusible form into an enol-keto-mixture; in the presence of light petroleum, the ketonic form melting at 110° is obtained. C. S.

Bromo- and Bromonitro-derivatives of *o*-Benzoylbenzoic Acid. FRANZ KUNCKELL and G. KNIGGE (*Ber.*, 1906, **39**, 194-196).—*Bromo-o-benzoylbenzoic acid*, $C_6H_4Br \cdot CO \cdot C_6H_4 \cdot CO_2H$, is obtained when *o*-benzoylbenzoic acid (Pechmann, *Abstr.*, 1881, 96) is heated with water and bromine (2 mols.) for five hours at 120° . It crystallises from alcohol, melts at 156° , and dissolves readily in most organic solvents. When heated for 10-20 minutes with 5-10 times its weight of fuming nitric acid, it yields *bromotetranitro-o-benzoylbenzoic acid*, $C_{14}H_5O_{11}N_4Br$, which crystallises from alcohol in pale yellow plates melting at 178° . When *o*-benzoylbenzoic acid is heated with water and bromine (3 mols.) at 180° , a mixture of mono- and dibromo-benzoylbenzoic acids and tetrabromobenzoic acid is obtained.

The *dibromo-o-benzoylbenzoic acid*, $C_{14}H_8O_3Br_2$, crystallises from benzene in colourless needles, melts at 194° , and is readily soluble in acetic acid, ether, or alcohol. The *tetrabromobenzoic acid* is sparingly soluble in alcohol, crystallises in yellow plates, and melts at 295° .

J. J. S.

Formation of Indigotin from Quinoline. HERMAN DECKER and C. KOPP (*Ber.*, 1906, **39**, 72).—If the additive product of quinoline with ethyl chloroacetate is oxidised with potassium permanganate, the filtrate rendered alkaline, evaporated, and heated at 200° , it is converted into indigotin. Formylphenylglycine-*o*-carboxylic acid, $CO_2H \cdot C_6H_4 \cdot N(CHO) \cdot CH_2 \cdot CO_2H$, is probably an intermediate product of the oxidation. T. M. L.

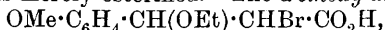
Influence of Alkyloxy-groups on the Reactivity of α -Bromine Atoms in Aromatic Compounds. ALFRED WERNER [with P. SCHORNDORFF and CH. CHOROWER] (*Ber.*, 1906, **39**, 27-36).—The presence of *o*- or *p*-alkyloxy-groups greatly facilitates the replace-

ment of α -halogen atoms by alkoxy- or phenoxy-groups, a reaction which has been frequently observed by Zincke in derivatives of *p*-hydroxybenzyl bromide, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Br} \rightarrow \text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OR}$, but not in benzyl bromide itself.

Thus, *o*-methylcoumaric dibromide, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$, when boiled with methyl alcohol, yields the α -methoxy-ester,



which separates from light petroleum in colourless crystals and melts at 64° ; the α -methoxy-acid, $\text{C}_{11}\text{H}_{13}\text{O}_4\text{Br}$, separates from light petroleum in colourless crystals and melts at 118° ; the potassium salt forms large, clear, square crystals with a blue fluorescence. The dibromide of cinnamic acid, $\text{C}_6\text{H}_5\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$, does not behave in this way, but is merely esterified. The α -ethoxy-acid,



separates from light petroleum in large, asymmetric crystals and melts at 103° . The α -isopropoxy-acid, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OPr}^i)\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$, separates from light petroleum in colourless prisms and melts at 125° . The action of phenol on methylcoumaric acid dibromide is more complex than that of alcohols; methyl bromide is apparently formed and α -*p*-hydroxyphenylcoumaran, $\text{O}\langle\text{C}_6\text{H}_4\rangle_{\text{CH}_2}\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, is the chief product; it crystallises from much hot water in minute, glistening flakes and melts at 150 – 154° . The acetyl derivative, $\text{C}_{16}\text{H}_{14}\text{O}_3$, crystallises from concentrated alcoholic solution in thin, glistening scales or broad needles, melts at 102° , and has a normal molecular weight when dissolved in acetic acid. The methyl ether crystallises from alcohol in thin scales and melts at 94 – 95° .

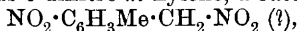
Anisylideneacetophenone dibromide, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{COPh}$, is acted on in a similar manner by methyl alcohol, the α -bromine atom being replaced by methoxyl. The α -methoxy-ketone,



separates from methyl alcohol in colourless needles and melts at 101° . The ethoxy-ketone, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OEt})\cdot\text{CHBr}\cdot\text{COPh}$, crystallises from alcohol in long, colourless needles and melts at 70° . The hydroxy-ketone, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CHBr}\cdot\text{COPh}$, prepared by boiling with aqueous acetone, crystallises from light petroleum in long, colourless needles and melts at 78° .

T. M. L.

2-Aminoisophthalic Acid. EMILIO NOELTING and CH. GACHOT (*Ber.*, 1906, 39, 73–76).—When boiled with nitric acid of sp. gr. 1.4, 2-nitro-*m*-xylene yields *v*-dinitro-*m*-xylene, a substance,



which changes readily into an aldehyde, and 2-nitro-*m*-toluic acid, $\text{C}_8\text{H}_7\text{O}_4\text{N}$, melting at 217.5 – 218° . When oxidised with potassium permanganate in alkaline solution, this yields 2-nitroisophthalic acid, $\text{C}_8\text{H}_5\text{O}_6\text{N}$, which is formed directly from 2-nitro-*m*-xylene by oxidation with potassium permanganate in presence of magnesium sulphate. It crystallises in white needles, commences to become brown at 287° , and is not completely melted at 300° . The barium salt was analysed; the dimethyl ester, $\text{C}_{10}\text{H}_9\text{O}_6\text{N}$, crystallises in glistening, white scales, melts at 129 – 130° , and undergoes partial hydrolysis when recrystal-

lised from boiling water. The *hydrochloride* of 2-aminoisophthalic acid, obtained by reduction of the nitro-acid with zinc and concentrated hydrochloric acid, crystallises in white needles and on exposure to the air readily loses hydrogen chloride, forming the free *amino-acid*, $C_8H_7O_4N$; this crystallises from alcohol in yellow leaflets, melts above 260° , and is easily soluble in alcohol or ether. The *copper* salt, $C_8H_5O_4NCu$, is obtained as a green precipitate, which, after drying at 119° , has the composition $2C_8H_5O_4NCu, CuO$.

2-Acetylaminoisophthalic acid, $NHAc \cdot C_6H_3(CO_2H)_2$, is prepared by oxidising aceto-*m*-2-xylylide with potassium permanganate in presence of magnesium sulphate; it crystallises in long, slender, white needles, and on prolonged boiling with concentrated hydrochloric acid yields the hydrochloride of 2-aminoisophthalic acid. When titrated with methyl-orange as indicator, the acid neutralises only 1 mol. of sodium hydroxide; the *copper* salt, $NHAc \cdot C_6H_3(CO_2)_2Cu$, was analysed.

When cooled and diazotised with sodium nitrite and hydrochloric acid or with nitrosyl sulphate and concentrated sulphuric acid and "coupled" with phenol in alkaline solution, 2-aminoisophthalic acid forms the *azo-derivative*, $C_6H_3(CO_2H)_2 \cdot N_2 \cdot C_6H_4 \cdot OH$, which is obtained in glistening, yellow, anhydrous scales or in red, spear-like needles containing $2/3H_2O$, which is lost at 115° . When dissolved in boiling water and allowed to cool slowly, the yellow modification is converted into the red; if this is heated with concentrated hydrochloric acid, it yields a yellow *product* which is insoluble in most solvents and cannot be reconverted into the red *azo-compound*. With *p*-cresol, diazotised 2-aminoisophthalic acid forms an *azo-derivative*, $C_{15}H_{12}O_5N_2$, which is obtained in two anhydrous modifications, red and yellow respectively.

G. Y.

Preparation of Chloro- and Bromo-phthalimides. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 161340).—The action of alkali hypochlorites on an aqueous suspension of phthalimide is very slow, whilst if the alkali salts of phthalimide are employed, partial hydrolysis to phthalamates occurs. If the phthalimide is suspended in acetic acid and sodium hypochlorite or hypobromite is added, chloro- or bromo-phthalimide is precipitated in a pure form.

C. H. D.

Synthesis of α -Amino-acids by means of Bromo-fatty Acids. EMIL FISCHER and WILHELM SCHMITZ (*Ber.*, 1906, 39, 351—356. Compare Fischer, *Abstr.*, 1904, i, 890).— α -Bromoisobutylmalonic acid, $C_7H_{11}O_4Br$, prepared by brominating isobutylmalonic acid (Guthzeit, *Abstr.*, 1882, 39), crystallises from benzene, melts at 139 — 141° (corr.), is readily soluble in water, alcohol, or ether, and when heated at its melting point under 12 mm. pressure evolves carbon dioxide and forms α -bromoisohexoic acid, $CHMe_2 \cdot CH_2 \cdot CHBr \cdot CO_2H$, which boils at 126 — 128.5° under 9 mm. pressure. With this is partially or wholly identical the bromoisohexoic acid formed by the action of bromine and phosphorus on isohexoic acid prepared from isoamyl cyanide.

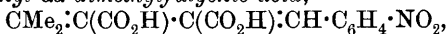
Ethyl γ -phenylethylmalonate, $CH_2Ph \cdot CH_2 \cdot CH(CO_2Et)_2$, formed by boiling ethyl sodiomalonate with ω -chloroethylbenzene in alcoholic

solution in a reflux apparatus, boils at 185—187° under 24 mm. pressure, and on hydrolysis with concentrated potassium hydroxide yields γ -phenylethylmalonic acid, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})_2$. This crystallises from toluene in glistening, colourless leaflets, melts and evolves carbon dioxide at 142—144° (corr.), and is readily soluble in hot water, alcohol, or ether.

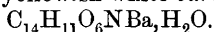
α -Bromo- γ -phenylethylmalonic acid, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CBr}(\text{CO}_2\text{H})_2$, formed by brominating γ -phenylethylmalonic acid, crystallises from benzene in small, nodular aggregates or from water in microscopic needles or thin prisms, and melts and decomposes at 116—118° (corr.). α -Bromo- γ -phenylbutyric acid, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$, crystallises from water in thin leaflets or from benzene in small, rectangular, thin plates, melts at 188—190° (corr.), and may be distilled, if rapidly heated, under 10 mm. pressure. When treated with 25 per cent. aqueous ammonia at 100° for one and a half hours or at the laboratory temperature for some days, it forms α -amino- γ -phenylbutyric acid, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$; this crystallises from boiling water in glistening needles or stellate aggregates of small plates containing H_2O , which is lost at 80° in a vacuum. When quickly heated, the dry amino-acid becomes yellow at 247° and melts and decomposes at about 252° (corr.); it has an unpleasant, bitter taste, and is moderately soluble in boiling alcohol. The *hydrochloride* crystallises from hot hydrochloric acid in glistening leaflets; the boiling aqueous solution of the base dissolves copper oxide, forming a blue solution, from which the *copper* salt crystallises on cooling in small, light blue needles or long, slender prisms.

G. Y.

Butadiene Compounds. XIV. Nitrophenyldimethylfulgenic Acids and their Yellow Fulgides. HANS STOBBE (*Ber.*, 1906, 39, 292—298. Compare this vol., i, 91, 92, 101).—[With KARL LEUNER.]
— δ -o-Nitrophenyl- $\alpha\alpha$ -dimethylfulgenic acid,



prepared from *o*-nitrobenzaldehyde and ethyl teraconate, crystallises from dilute alcohol or 80 per cent. acetic acid; it is white with a yellow lustre and gives a yellowish-white *barium* salt,



The corresponding *fulgide*, $\text{C}_{14}\text{H}_{11}\text{O}_5\text{N}$, prepared by means of acetyl chloride, crystallises from benzene with $\frac{1}{2}\text{C}_6\text{H}_6$ in bright yellow, lustrous leaflets and melts and decomposes at 155°.

δ -*m*-Nitrophenyl- $\alpha\alpha$ -dimethylfulgenic acid, prepared in similar manner from *m*-nitrobenzaldehyde, crystallises from ether, acetic acid, or dilute alcohol, and is bright yellow in colour with a green tinge; it melts at 228° and gives a white *barium* salt, $\text{C}_{14}\text{H}_{11}\text{O}_6\text{NBa}\cdot\text{H}_2\text{O}$. The *fulgide*, $\text{C}_{14}\text{H}_{11}\text{O}_5\text{N}$, crystallises from benzene either with C_6H_6 in large, well-formed, intensely yellow prisms, or in smaller yellow prisms not containing the solvent; both forms melt at 120.5°.

δ -*p*-Nitrophenyl- $\alpha\alpha$ -dimethylfulgenic acid, prepared by means of *p*-nitrobenzaldehyde, crystallises from ether or dilute alcohol, has a feebly yellow colour with a brown lustre, and melts and decomposes at 234°; the *barium* salt, $\text{C}_{14}\text{H}_{11}\text{O}_6\text{NBa}\cdot\text{H}_2\text{O}$, has a greenish-yellow

colour which becomes yellow at 180° . The *fulgide* separates from benzene in orange-red crystals with C_6H_6 , which rapidly effloresce, giving a bright orange-coloured powder similar in shade to lead iodide; from chloroform, long, yellow needles are obtained. The fulgide melts at $175-177^{\circ}$.

A table is given showing the relationships of colour presented by α -dimethylfulgenic acid, its *o*-, *m*-, and *p*-nitrophenyl derivatives and their fulgides, and analogous derivatives of $\alpha\alpha\delta$ -triphenylfulgenic acid. The relation between colour and constitution is discussed in these cases.

W. A. D.

Sulphonic Derivatives of Naphthalic Anhydride. GUIDO BARGELLINI (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 688—696. Compare Francesconi and Bargellini, *Abstr.*, 1903, i, 34).—The blue fluorescence exhibited by a solution of naphthalic anhydride in concentrated or fuming sulphuric acid is not due to the formation of any compound in the solution. If the liquid is kept for several months, the fluorescence diminishes continuously and sulphonaphthalic acid is formed. This change proceeds more rapidly on heating, and at temperatures above 100° disulphonaphthalic acid is also formed. Neither of these compounds exhibits fluorescence.

When fused with potassium hydroxide, sulphonaphthalic acid (Anselm and Zuckmayer, *Abstr.*, 1900, i, 175) yields the hydroxynaphthalic anhydride melting at 287° . Since this anhydride has also been obtained from a 3-nitronaphthalic anhydride (Anselm and Zuckmayer, *loc. cit.*), and since also 4-hydroxynaphthalic anhydride melts at 257° (Graebe, *Abstr.*, 1903, i, 408), sulphonaphthalic acid must have the sulphonic group in the 3-position, the two carboxyl groups being at positions 1 and 8.

Disulphonaphthalic acid, $C_{10}H_4(CO_2H)_2(SO_3H)_2$ [$(CO_2H)_2 : (SO_3H)_2 = 1 : 8 : 2 : 6$], melts at about 220° and is readily soluble in water. The *barium* salt crystallises from water with $4H_2O$, and is precipitated, by addition of alcohol to its aqueous solution, as the dihydrate. The *anilide*, $C_{24}H_{14}O_6N_2S_2$, crystallises from alcohol in colourless plates decomposing at above 290° and is readily soluble in methyl alcohol and slightly so in ether, benzene, or carbon disulphide.

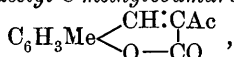
4:5-Dibromo-3-sulphonaphthalic acid, $C_{10}H_3Br_2(CO_2H)_2 \cdot SO_3H$, prepared by the action of bromine on a fuming sulphuric acid solution of naphthalic anhydride, crystallises from a mixture of ethyl acetate and ether in white needles melting at $204-205^{\circ}$, and dissolves in water, nitric acid, acetic acid, methyl, ethyl, or amyl alcohol, or dilute solutions of the alkali hydroxides or carbonates, and to a slight extent in benzene or carbon disulphide; it dissolves also in ammonia solution, giving a yellow liquid which deposits yellow, silky needles on cooling. Not one of these solutions, or that in concentrated sulphuric acid, is fluorescent. The *barium* salt, $C_{24}H_6O_{14}Br_4S_2Ba_3 \cdot 8H_2O$, crystallises from water in white needles. The solution of the barium salt gives with copper acetate a greenish-blue, gelatinous precipitate, with lead acetate a white, flocculent precipitate, and with silver nitrate a white precipitate which blackens in the air.

T. H. P.

New Coumarins and some of their Derivatives. PH. CHUIT and FR. BOLSING (*Bull. Soc. chim.*, 1906, [iii], 35, 76—90).—These coumarins and their derivatives were prepared by condensing hydroxyaldehydes with the appropriate ketonic acid or ester in presence of an amine, usually aniline or piperidine, a reaction first employed by Knoevenagel (*Abstr.*, 1899, i, 116).

8-*Methylcoumarincarboxylic acid*, $C_6H_3Me \begin{smallmatrix} \text{CH}:\text{C}\cdot\text{CO}_2\text{H} \\ \text{O}-\text{CO} \end{smallmatrix}$, prepared by

condensing 3-methylsalicylaldehyde with malonic acid in presence of aniline hydrochloride, crystallises from benzene in colourless needles, melts at 142—143°, is readily soluble in hot benzene or acetic acid, soluble in alcohol (2.28 grams in 100 c.c. at 14°) and boiling water, slightly so in hot petroleum. The *ethyl* ester, obtained by using ethyl malonate in the condensation, forms colourless crystals, is inodorous, and melts at 81°. 8-*Methylcoumarin*, obtained by heating the acid, separates from alcohol in long, colourless needles, melts at 109—110°, boils at 178° under 20 mm. pressure, and has a feeble odour of coumarin. When ethyl acetoacetate is used in place of ethyl malonate in the condensation, 3-*acetyl*-8-*methylcoumarin*,



is formed: this crystallises in brilliant, flattened, faintly yellow needles, is inodorous, and melts at 125.8—126.2°. The *phenylhydrazone* forms short, yellow tinted needles and melts at 168—169°; the *oxime*, yellowish-white needles melting and decomposing at 212—213°, and the *semicarbazone*, small, yellow crystals which melt and decompose at 224—225°.

When the Tiemann-Schotten reaction is applied to *m*-cresol, in addition to the *p*-aldehyde, 4-methylsalicylaldehyde (m. p. 59°) and 6-methylsalicylaldehyde (m. p. 31.5°) are produced. From the former, 7-*methylcoumarincarboxylic acid* was prepared: this crystallises in colourless leaflets, melts at 198.8—199.8°, is soluble in boiling acetic acid, slightly so in alcohol (0.45 gram in 100 c.c. at 14°) and in boiling water. The *ethyl* ester forms colourless, nacreous spangles from dilute alcohol, melts at 101.5—102.5°, and is readily soluble in warm alcohol, slightly so in light petroleum. 7-*Methylcoumarin*, obtained by heating the acid at 250—300°, crystallises from a mixture of alcohol and water in colourless leaflets, melts at 125.8—126.4°, boils at 171.5° under 11 mm. pressure, and possesses a strong odour of coumarin (compare Schmidt, *Inaug. Diss. Rostock*). 3-*Acetyl*-7-*methylcoumarin*, prepared by condensing the aldehyde with ethyl acetoacetate in presence of piperidine, crystallises from alcohol in brilliant, colourless needles, melts at 156—157°, and is inodorous; the *oxime* separates from alcohol in yellow needles and melts and decomposes at 224°.

5-*Methylcoumarincarboxylic acid*, similarly prepared from 6-methylsalicylaldehyde, crystallises from alcohol in colourless leaflets and melts at 162.5—163°; its solubility in alcohol is 1 gram in 100 c.c. at 14°. The *ethyl* ester crystallises from dilute alcohol in brilliant, colourless needles and melts at 122—122.5°. 5-*Methylcoumarin*, produced by heating the acid at 260°, crystallises from water in long needles,

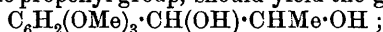
possesses a faint coumarin odour, and melts at $65-65.8^{\circ}$. 3-Acetyl-5-methylcoumarin forms yellow needles, melts at 115° , and is easily soluble in warm alcohol. The *oxime* crystallises in white needles and melts and decomposes at 214° .

6-Methylcoumarincarboxylic acid, prepared similarly from 5-methylsalicylaldehyde, crystallises from alcohol in yellowish-white needles, melts at 166.8° , and is soluble in acetic acid, less so in alcohol (1.22 grams in 100 c.c. at 14°). The *ethyl* ester separates from alcohol in large, colourless tables, is inodorous, melts at $103-104^{\circ}$, and is readily soluble in benzene, soluble in alcohol, and slightly so in water or light petroleum. 6-Methylcoumarin forms colourless needles from alcohol, melts at $74.6-75^{\circ}$, and boils at 303° under 725 mm. and at 174° under 14 mm. pressure. Its odour is slightly different from and more persistent than that of coumarin. 3-Acetyl-6-methylcoumarin separates on cooling a solution in warm alcohol in yellowish-white, nacreous leaflets and melts at $128-128.4^{\circ}$. The *phenylhydrazone* melts at $193-194^{\circ}$, the *oxime*, with decomposition, at 219° , and the *semicarbazone* at 211° , also with decomposition.

T. A. H.

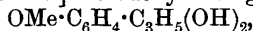
Action of Aqueous Solutions of Mercuric Acetate on Olefinic Compounds. LUIGI BALBIANO [with VINCENZO PAOLINI, A. NARDACCI, U. TONAZZI, ENRICO LUZZI, F. BERNARDINI, D. CIRELLI, G. MAMMOLA, and GION VESPIGNANI] (*Mem. R. Accad. Lincei*, 1905, [v], 5, 515-578).—The greater part of this work has been already published (see Abstr., 1902, i, 808; ii, 109; 1904, i, 72 and 261), the new matter being as follows.

[With D. CIRELLI].—The action of mercuric acetate on asarone, which contains the propenyl group, should yield the glycol,



if this compound is formed, it loses water, giving the *aldehyde*, $\text{C}_6\text{H}_2(\text{OMe})_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHO}$, which boils at 184° under 14 mm. pressure and solidifies in lamellated aggregates melting at $47-48^{\circ}$. The *semicarbazone*, $\text{C}_{13}\text{H}_{15}\text{O}_4\text{N}_2$, crystallises from alcohol in shining plates melting at $157-158^{\circ}$.

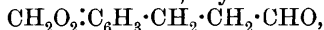
[With VINCENZO PAOLINI].—On dehydrating the glycol,



prepared by the action of mercuric acetate on anethole (Abstr., 1902, i, 808), by means of zinc chloride, it is converted into β -p-methoxyphenylpropaldehyde, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHO}$, which is a pale yellow liquid with a faint, aromatic odour, is soluble in alcohol or ether, and boils at $132-135^{\circ}$ under 10 mm. pressure. The *semicarbazone*, $\text{C}_{11}\text{H}_{15}\text{O}_2\text{N}_2$, crystallises from alcohol in superposed laminae, melts at 174° , and is soluble in all organic solvents. The *semicarbazone* of the isomeric aldehyde obtained by Bougault by the action of iodine and yellow mercuric oxide on anethole (Abstr., 1902, i, 452) crystallises from alcohol in feathery aggregates of white, opaque needles melting at 134° , and is soluble in all the organic solvents. On treating β -p-methoxyphenylpropaldehyde in strongly alkaline alcoholic solution with benzenesulphohydroxamic acid (compare Rimini, Abstr., 1901, i, 450) and afterwards neutralising the cold solution with acetic acid and

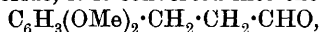
treating with copper acetate, the compound, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_3\text{H}_4 \cdot \text{C} \begin{smallmatrix} \text{NO} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix} \text{Cu}$, is obtained as a green powder slightly soluble in alcohol. On oxidation with moist silver oxide in presence of sodium hydroxide, β -*p*-methoxyphenylpropaldehyde yields a large proportion of resinous matter and a small quantity of anisic acid, whilst *p*-methoxyhydratropaldehyde (Bougault, *loc. cit.*) gives an almost quantitative yield of *p*-methoxyhydratropic acid.

When the glycol, $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CHMe} \cdot \text{OH}$, obtained by the action of mercuric acetate on *isofafrole* (Abstr., 1902, i, 808) is dehydrated by means of zinc chloride, it yields the aldehyde,

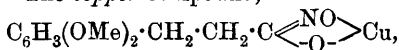


which is a pale yellow liquid with a penetrating aromatic odour and boils at $145\text{--}150^\circ$ under 22 mm. pressure. The *oxime*, $\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}$, crystallises from aqueous alcohol in faintly yellow, prismatic needles melting at 89° . The *semicarbazone*, $\text{C}_{11}\text{H}_{11}\text{O}_3\text{N}_3$, crystallises from aqueous alcohol in white laminae melting at 158° . On treatment with benzenesulphohydroxamic acid and subsequent neutralisation with acetic acid, it gives on addition of copper acetate (*vide supra*) the compound $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{C}_2\text{H}_4 \cdot \text{C} \begin{smallmatrix} \text{NO} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix} \text{Cu}$, in the form of a bluish-green powder. When oxidised with silver oxide in presence of sodium hydroxide solution, the aldehyde is mainly resinified, but yields a small quantity of piperonylic acid; the isomeric 3:4-methylenedioxyhydratropaldehyde (Bougault, Abstr., 1901, i, 721) yields 3:4-methylenedioxyhydratropic acid.

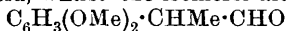
On dehydrating the glycol, $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{C}_3\text{H}_5(\text{OH})_2$, obtained by the action of mercuric acetate on methyl *isoeugenole* (Abstr., 1904, i, 72), by means of zinc chloride, it is converted into the aldehyde,



which is a pale yellow, oily liquid with a faint, aromatic odour, is soluble in alcohol or ether, and boils at $146\text{--}147^\circ$ under 6 mm. pressure. The *semicarbazone*, $\text{C}_{12}\text{H}_{17}\text{O}_3\text{N}_3$, crystallises from alcohol in silky, white needles melting at $176\text{--}177^\circ$; the *oxime*, $\text{C}_{11}\text{H}_{15}\text{O}_3\text{N}$, crystallises from alcohol in radiating laminae melting at $62.5\text{--}63^\circ$ and is soluble in ether. The copper compound,



has been prepared. On oxidation with silver oxide in presence of sodium hydroxide, the aldehyde mostly resinifies but gives a small quantity of veratric acid, whilst the isomeric aldehyde,



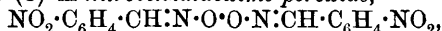
(Bougault, Abstr., 1902, i, 452), yields 3:4-dimethoxyhydratropic acid.

T. H. P.

Oxidation of Aromatic Aldoximes with Amyl Nitrite.
GAETANO MINUNNI and ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 518—525).—Oxidation of benzaldoxime by means of amyl nitrite in ethereal solution yields: (1) azobenzenyl peroxide (benzaldoxime peroxide), $\text{CHPh} \cdot \text{N} \cdot \text{O} \cdot \text{O} \cdot \text{N} \cdot \text{CHPh}$, which was obtained by Beckmann by oxidising benzaldoxime with potassium ferricyanide (Abstr.,

1889, 980), and melts and decomposes at 96° , not at 105° , as Beckmann stated; (2) dibenzénylazoxime, $\begin{matrix} \text{CPh:N} \\ \text{N:CPh} \end{matrix} > \text{O}$, which has the melting point $102.5\text{--}104^\circ$, and not 108° , as stated in the literature; (3) benzildioxime peroxide, $\begin{matrix} \text{CPh:N}\cdot\text{O} \\ \text{CPh:N}\cdot\text{O} \end{matrix}$; (4) a small quantity of a compound crystallising from alcohol in colourless needles melting at $152\text{--}153^\circ$.

m-Nitrobenzaldoxime, on oxidation in ethereal solution with amyl nitrite, yields: (1) *m*-nitrobenzaldoxime peroxide,



which crystallises from a mixture of chloroform and alcohol in shining plates melting and decomposing at 105° ; (2) di-*m*-nitrobenzenylazoxime, which was described by Stieglitz (Abstr., 1890, 254) and melts at 168° , the melting point 138° , given by Krümmel (Abstr., 1895, i, 661), being erroneous; the compound described by Bamberger and Scheutz (Abstr., 1901, i, 548) as di-*m*-nitrobenzenylazoxime has some other structure.

T. H. P.

Chlorodinitrobenzophenone and its Conversion into Dinitrophenylacridine Derivatives. FRITZ ULLMANN and J. BROID (Ber., 1906, 39, 356—370). Compare Ullmann and Ernst, this vol., i, 205).—2-Chloro-3:5-dinitrobenzophenone, $\text{C}_{13}\text{H}_7\text{O}_5\text{N}_2\text{Cl}$, formed by the action of 2-chloro-3:5-dinitrobenzoyl chloride on benzene in presence of aluminium chloride, crystallises from glacial acetic acid in long, slightly yellow needles and melts at 149° . On treatment with sodium hydroxide in boiling alcoholic solution, it yields the sodium derivative of 3:5-dinitro-2-hydroxybenzophenone, which crystallises in orange-yellow needles, decomposes at about 318° , and has a bitter taste; the hydroxy-compound, $\text{C}_{13}\text{H}_8\text{O}_6\text{N}_2$, crystallises in small, yellow needles, melts at 116° , is soluble in benzene, ether, glacial acetic acid, or boiling alcohol, and gives a light yellow coloration with concentrated sulphuric acid and an intense yellow with dilute sodium hydroxide. 3:5-Dinitro-2-methoxybenzophenone, $\text{OMe}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{COPh}$, formed in a poor yield by the action of sodium methoxide on the chloro-compound, crystallises in a colourless mass and melts at 83° .

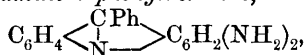
The action of anhydrous ammonia on 2-chloro-3:5-dinitrobenzophenone in boiling amyl-alcoholic solution leads to the formation of 3:5-dinitro-2-aminobenzophenone, $\text{NH}_2\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{COPh}$, which crystallises in yellowish-brown needles, melts at 166° , and when treated with sodium nitrite in concentrated sulphuric acid solution at the ordinary temperature and finally at $80\text{--}85^\circ$ yields 2:4-dinitrofluorenone, $\text{CO} < \begin{matrix} \text{C}_6\text{H}_2(\text{NO}_2)_2 \\ \text{C}_6\text{H}_4 \end{matrix}$. This crystallises from boiling glacial

acetic acid in stellate aggregates of yellow needles, melts at 197° , and dissolves readily in benzene or chloroform, forming a yellow solution. 3:5-Dinitro-2-ethylaminobenzophenone, $\text{C}_{15}\text{H}_{13}\text{O}_5\text{N}_3$, formed by the action of ethylamine on 2-chloro-3:5-dinitrobenzophenone in alcoholic solution, crystallises in glistening, lemon-yellow leaflets, melts at 104° , and is readily soluble in benzene, chloroform, or hot alcohol, ether,

or glacial acetic acid. When heated with copper powder and nitrobenzene at 200° , 2-chloro-3:5-dinitrobenzene forms 1:1'-*dibenzoyl*-3:3':5:5'-*tetranitrodiphenyl*, $\text{COPh}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{COPh}$, which melts at 186° .

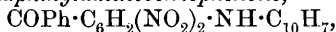
3:5-*Dinitro-2-anilinobenzophenone*, $\text{NHPh}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{COPh}$, is formed by fusing 2-chloro-3:5-dinitrobenzophenone with aniline and dissolving the product in alcohol; it crystallises in small, glistening, orange-red needles, melts at 206° , and on prolonged heating with aniline yields 1:3-*dinitro-5-phenylacridine*, $\text{C}_6\text{H}_4\langle\text{CPh}\rangle\text{N}\text{C}_6\text{H}_2(\text{NO}_2)_2$,

which crystallises in lemon-yellow needles, melts at 240° , and dissolves in concentrated sulphuric or hydrochloric acid to form a yellow solution, from which the base separates in a yellow, flocculent precipitate on dilution. When reduced with stannous chloride and hydrochloric acid, it forms 1:3-*diamino-5-phenylacridine*,



which is isolated as the *nitrate*, $\text{C}_{19}\text{H}_{15}\text{N}_3\cdot\text{HNO}_3$; this crystallises from dilute acetic acid and dissolves in boiling alcohol to form a yellowish-brown solution having a slight green fluorescence. The *base* forms orange-yellow to brown crystals, melts at 159° , and dissolves in alcohol, forming an orange-yellow solution with slight green fluorescence, or in concentrated sulphuric acid, forming a yellow solution with brilliant green fluorescence; the orange solution in concentrated hydrochloric acid becomes red when diluted with water. 1:3-*Diacetyl-amino-5-phenylacridine* crystallises in yellowish-brown needles, melts at $232\text{--}233^{\circ}$, and dissolves in concentrated sulphuric acid to form a yellow solution with green fluorescence.

3:5-*Dinitro-2- α -naphthylaminobenzophenone*,

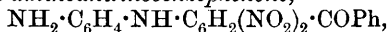


crystallises from glacial acetic acid in glistening, orange-red needles, melts at 190° , and when heated with concentrated sulphuric acid at $90\text{--}100^{\circ}$ forms 9:11-*dinitro-7-phenyl-2:1-phenonaphthacridine*,

$\text{C}_{10}\text{H}_6\langle\text{CPh}\rangle\text{N}\text{C}_6\text{H}_2(\text{NO}_2)_2$, which separates in yellow crystals, melts at 315° , is soluble in hot benzene or chloroform, and dissolves in concentrated sulphuric acid to form an orange-red solution; this on dilution deposits the base as a yellow, flocculent precipitate.

3:5-*Dinitro-2- β -naphthylaminobenzophenone*, $\text{C}_{23}\text{H}_{15}\text{O}_5\text{N}_3$, crystallises in orange-red needles, melts at 208° , and is moderately soluble in chloroform or glacial acetic acid, forming yellow solutions. 9:11-*Dinitro-7-phenyl-1:2-phenonaphthacridine*, $\text{C}_{23}\text{H}_{13}\text{O}_4\text{N}_3$, forms yellow crystals and melts at 320° .

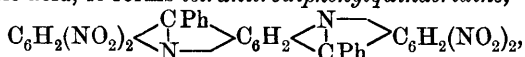
3:5-*Dinitro-2-p-aminoanilinobenzophenone*,



formed by the action of an excess of *p*-phenylenediamine on 2-chloro-3:5-dinitrobenzophenone, crystallises from toluene in glistening, reddish-brown needles and melts at 221° . 1:3-*Dinitro-7-amino-5-phenylacridine*,

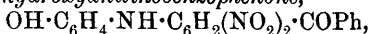
$\text{NH}_2\cdot\text{C}_6\text{H}_3\langle\text{CPh}\rangle\text{N}\text{C}_6\text{H}_2(\text{NO}_2)_2$, crystallises from aniline in reddish-violet needles and melts above 360° .

3':5':3'':5''-Tetranitro-1':1''-dibenzoyldiphenyl-1:4-phenylenediamine, $C_6H_4[NH \cdot C_6H_2(NO_2)_2 \cdot CPh]_2$, is formed together with 3:5-dinitro-2-*p*-aminoanilinobenzophenone by the interaction of 2-chloro-3:5-dinitrobenzophenone and *p*-phenylenediamine in molecular proportions; it crystallises in glistening, scarlet leaflets, melts at 318° , and dissolves in concentrated sulphuric acid, forming a reddish-brown solution. When heated at 100° with concentrated sulphuric acid and glacial acetic acid, it forms *tetranitrodiphenylquinacridine*,



which is precipitated from its solution in boiling aniline by alcohol as a brown powder and dissolves sparingly in boiling toluene or glacial acetic acid.

3:5-Dinitro-2-*o*-hydroxyanilinobenzophenone,



crystallises in glistening, yellow leaflets, melts at 233° , and dissolves in aqueous sodium hydroxide, forming a reddish-brown, or in concentrated sulphuric acid forming a wine-red, solution. 1:3-Dinitro-9-

hydroxy-5-phenylacridine, $OH \cdot C_6H_3 \left\langle \begin{array}{c} CPh \\ N \end{array} \right\rangle C_6H_2(NO_2)_2$, forms a reddish-brown powder, melts at 233° , is readily soluble in chloroform, and dissolves in concentrated sulphuric acid, forming a red, or in aqueous sodium hydroxide forming a reddish-brown, solution.

The action of aqueous sodium hydroxide on 3:5-dinitro-2-*o*-hydroxyanilinobenzophenone in boiling alcoholic solution leads to the formation of 3-nitro-5-benzoylphenoxazine, $C_6H_4 \left\langle \begin{array}{c} O \\ NH \end{array} \right\rangle C_6H_2(NO_2) \cdot CPh$, which crystallises from amyl alcohol or toluene in red needles, melts at 217° , and is readily soluble in boiling benzene or chloroform, but only sparingly so in boiling alcohol or ether. It dissolves in alcohol containing a few drops of concentrated aqueous sodium hydroxide to form a blue solution, from which it is precipitated unchanged on dilution with water; in concentrated sulphuric acid, it dissolves to form a red solution, which becomes blue when warmed. G. Y.

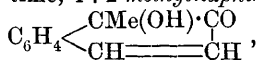
1-Methyl- β -naphthol and its Quinonoid Derivatives. K. FRIES and EDUARD HÜBNER (*Ber.*, 1906, 39, 435—453. Compare Zincke, *Abstr.*, 1903, i, 756).—Di- β -naphthylmethane is most readily prepared by the condensing action of sodium acetate on an alcoholic solution of β -naphthol and formaldehyde, and is converted by nitrous acid into the *diquinonitrole*, $CH_2 \left[C(NO_2) \left\langle \begin{array}{c} C_6H_4 \\ CO \cdot CH \end{array} \right\rangle CH \right]_2$, which crystallises in pale yellow plates melting- and decomposing at 115° . It dissolves readily in acetone, chloroform, or ether, sparingly in benzene or alcohol, and is insoluble in alkalis. It is decomposed when boiled with a mixture of ether and glacial acetic acid, and when reduced with zinc and hydrochloric acid yields dinaphthylmethane. When warmed with an acetic acid solution of hydrogen chloride at 60° , the hydrocarbon yields a brown, crystalline compound, which is transformed into dinaphthaxanthene when dissolved in acetone and precipitated with water.

Dinaphthylmethane is readily decomposed by sodium hydroxide

solution and zinc dust, yielding β -naphthol and 1-methyl- β -naphthol, $C_{10}H_6Me \cdot OH$; the amount of the methyl-naphthol may be increased by adding formaldehyde and again heating with zinc dust and repeating the operations several times. It may be separated from dinaphthylmethane by means of its solubility in hot water. It crystallises in colourless needles, melts at 110° , dissolves readily in most organic solvents, and is volatile in steam. It does not couple with diazonium salts and is oxidised by nitric acid to phthalic acid. The *acetyl* derivative, $C_{13}H_{12}O_2$, crystallises from light petroleum in long, flat prisms melting at 66° . The *methyl ether* crystallises in colourless plates melting at 39° , and the *ethyl ether* also in plates melting at 50° . 6-Bromo-1-methyl- β -naphthol, $C_{10}H_5MeBr \cdot OH$, crystallises from benzene in colourless needles melting at 129° , and when oxidised yields 4-bromophthalic acid. The *ethyl ether*, $C_{10}H_5MeBr \cdot OEt$, melts at 66° , and the *acetyl* derivative, $C_{10}H_5MeBr \cdot OAc$, at 88° . 3:6-Dibromo-1-methyl- β -naphthol, $C_{10}H_4MeBr_2 \cdot OH$, forms colourless needles, melts at 180° , and dissolves readily in cold ether, acetone, or chloroform; it also dissolves in aqueous sodium hydroxide, but is precipitated on the addition of much water. When oxidised, it yields 4-bromophthalic acid. The *acetyl* derivative, $C_{10}H_4MeBr_2 \cdot OAc$, melts at 154° .

1-Methyl- β -naphthylamine, obtained by the action of calcium chloride ammonia on the naphthol at 270° , crystallises from light petroleum in colourless needles melting at 51° . It dissolves readily in most organic solvents, yields a sparingly soluble *sulphate* and an *acetyl* derivative, $C_{10}H_6Me \cdot NHAc$, melting at 189° .

Nitrous acid converts methyl- β -naphthol into 1:2-methylnaphthaquinonitrole, $C_6H_4 \begin{smallmatrix} \text{CMe}(\text{NO}_2) \cdot \text{CO} \\ \text{CH} = \text{CH} \end{smallmatrix}$, which crystallises from benzene in colourless, flat needles melting at 60° . When rapidly heated, it decomposes at 140° , evolving nitric oxide; it is readily soluble in the ordinary organic solvents, and when reduced yields methyl- β -naphthol. When its solution in a mixture of glacial acetic acid and ether is heated at 70° for some time, 1:2-methylnaphtha- ψ -quinol,



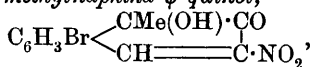
is obtained. It crystallises from water in glistening, colourless plates melting at 89° , and is readily soluble in most organic solvents. The *acetyl* derivative melts at 130° . 1:2-Naphthamethylenequinone

(β -naphthaquinone 1-methide), $C_6H_4 \begin{smallmatrix} \text{C}(\text{CH}_2) \cdot \text{CO} \\ \text{CH} = \text{CH} \end{smallmatrix}$, is obtained when

sodium nitrite is added slowly to a glacial acetic acid solution of methyl-naphthol, the mixture kept for eight hours, and then poured into cold water. It crystallises from light petroleum in compact, yellow needles, melts at 132° , and is insoluble in alkalis. When boiled for some time with alcohol, water, or acetone, it is converted into products which dissolve in alkalis.

6-Bromo-1:2-methylnaphthaquinonitrole, $C_6H_3Br \begin{smallmatrix} \text{CMe}(\text{NO}_2) \cdot \text{CO} \\ \text{CH} = \text{CH} \end{smallmatrix}$, crystallises in flat, compact needles, melts and decomposes at 99° , and when reduced yields bromomethylnaphthol. 6-Bromo-1:2-methyl-

naphtha-ψ-quinol, $C_{11}H_9O_2Br$, crystallises in yellow plates, melts at 84° , and is readily soluble in most organic solvents, but dissolves only slowly in alkalis. The *acetyl* derivative, $C_{13}H_{11}O_3Br$, melts at 101° . 6-Bromo-3-nitro-1:2-methylnaphtha-ψ-quinol,



obtained by the action of nitric acid on the bromoquinonitrole or on bromomethylnaphthol, crystallises in golden-yellow plates, melts at 155° , and is only moderately soluble in ether, alcohol, benzene, or acetic acid. It dissolves in alkali hydroxides at the ordinary temperature. When reduced with sulphurous acid in acetic acid solution, it yields 6-bromo-

3-nitro-1-methyl-β-naphthol, $C_6H_3Br \begin{cases} CMe \cdot C \cdot OH \\ CH : CNO_2 \end{cases}$, which crystallises in

orange-red needles melting at 163° . This dissolves in hot sodium carbonate solution, yielding a violet-black coloured liquid, from which the unaltered naphthol crystallises on cooling. The *sodium* salt forms long, blackish-violet needles, but is hydrolysed by water. The alkali salts of methylnaphthol and of its bromo-derivative, and also the alkali salts of bromoaminomethylnaphthol, are not hydrolysed in the same manner, and it is suggested that the nitro-compound may have the

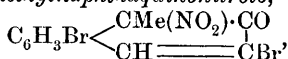
ketonic constitution $C_6H_3Br \begin{cases} CHMe \cdot CO \\ CH = C \cdot NO_2 \end{cases}$. 6-Bromo-3-amino-1-methyl-

β-naphthol, obtained by reducing the nitrobromoquinonitrole with zinc and hydrochloric acid, crystallises from benzene in slender, colourless needles melting at 163° . It dissolves readily in ether, acetone, or alkali hydroxides. The *monoacetyl* derivative, $C_{13}H_{12}O_2NBr$, crystallises in colourless needles melting at 183° , and the *diacetyl* derivative in needles melting at 240° . With nitrous acid, the aminophenol yields a yellow diazophenol anhydride.

6-Bromo-1:2-naphthamethylenequinone (6-bromo-β-naphthaquinone-1-methide), $C_6H_3Br \begin{cases} C(CH_2) \cdot CO \\ CH = CH \end{cases}$, crystallises from light petroleum in

yellow plates melting at 144° . It forms an *additive* compound with acetyl chloride, $C_{13}H_{10}O_2ClBr$, which forms compact needles melting at 158° .

3:6-Dibromo-1:2-methylnaphthaquinonitrole,



crystallises in colourless, flat needles melting at 130° and is the most stable of the *o*-quinonitroles. With acetic acid, it is slowly transformed

into 3:6-dibromo-1:2-methylnaphtha-ψ-quinol, $C_6H_3Br \begin{cases} CMe(OH) \cdot CO \\ CH = CBr \end{cases}$,

which crystallises in colourless needles melting at 101° . The *acetyl* derivative melts at 152° .
J. J. S.

Constitution of Alizarin Monomethyl Ethers. HERMAN DECKER and ED. LAUBE (*Ber.*, 1906, **39**, 112—116, 526).—1-Chloro-2-hydroxyanthraquinone, $C_6H_4 \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} C_6H_2Cl \cdot OH$, is formed by boiling 2-hydroxyanthraquinone, which melts at 306° (corr.), with sodium hypochlorite in aqueous sodium hydroxide solution (Wedekind, D.R.-P.

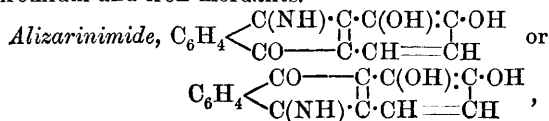
152172); it crystallises in small, yellow needles, or on slow evaporation of its solutions in rosettes of needles, melts at 226° (corr.), and dissolves in aqueous alkali hydroxides or carbonates to form red solutions; the *potassium* derivative is insoluble in cold water, but dissolves in alcohol, forming a violet solution. When fused with sodium ethoxide, it forms alizarin, and when heated with ammonia under pressure yields an *amino*-compound melting at 240 – 245° (corr.).

1-Chloro-2-acetoxyanthraquinone, $C_{14}H_6O_3ClAc$, formed by boiling the hydroxy-compound with acetic anhydride containing one to two drops of concentrated sulphuric acid, crystallises from alcohol in yellow, flocculent aggregates, melts at 163.5° , is hydrolysed only slowly by boiling aqueous alkali hydroxides, and dissolves in concentrated sulphuric acid, forming a red solution.

1-Chloro-2-methoxyanthraquinone, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} C_6H_2Cl \cdot OMe$, is prepared by heating the sodium derivative of 1-chloro-2-hydroxyanthraquinone with methyl sulphate at 140° ; after recrystallisation from alcohol or benzene, it melts at 223 – 224° (corr.). It is easily soluble in hot amyl alcohol or in concentrated sulphuric acid, forming an orange-red solution, and when heated with aqueous sodium hydroxide under pressure yields chiefly alizarin. When heated with sodium methoxide in methyl-alcoholic solution in a sealed tube at 100° for twelve hours, it yields alizarin monomethyl ether [1-hydroxy-2-methoxyanthraquinone], melting at 232 – 233° (Schunck and Marchlewski, *Trans.*, 1894, 65, 185).

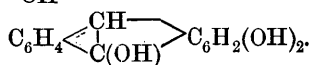
When heated with sodium ethoxide and ethyl alcohol, 1-chloro-2-methoxyanthraquinone yields a mixture of 1-hydroxy-2-methoxy- and 1-ethoxy-2-methoxy-anthraquinone; these are separated by treatment with benzene and aqueous sodium hydroxide. The monomethyl ether, melting at 232 – 233° , is obtained on acidification of the alkaline solution, whilst 1-ethoxy-2-methoxyanthraquinone crystallises from the benzene solution and melts at 169 – 170° . G. Y.

Reduction Products of Hydroxyanthraquinones. MAURICE PRUD'HOMME (*Bull. Soc. chim.*, 1906, [iii], 35, 71–76).—When freshly precipitated alizarin, anthrapurpurin, or flavopurpurin is suspended in dilute acid and zinc dust is added, a brown or olive-green reduction product is formed, depending on the conditions of the experiment. Each of these reduction products is convertible into the same yellow substance by the action of acids. All three substances dissolve in alkalis to form solutions which are redder, but less intense, than that given by alizarin; they dye with the usual mordants in neutral solution, giving tints similar to those produced by alizarin, but in presence of acetic acid, owing apparently to the reduction of the mordant by the dyes, they give feeble tints or none at all with chromium and iron mordants.



is prepared by heating alizarin with ammonia solution under pressure (Farbenfabriken vorm. Fr. Bayer & Co.). It crystallises from pyridine and when warmed with alkalis or acids is resolved into its generators. With aniline or phenylhydrazine, the imino-group is replaced by :NPh or :N.NHPh.

Alizarinimide is also produced when the precipitate, obtained by acidifying the brown solution, produced by the reduction of alizarin with hot ammonia solution and zinc dust, is washed, redissolved in ammonia, and oxidised by exposure to air. If, however, the brown solution itself is exposed to air, it also re-oxidises, forming the isomeride of alizarinimide represented by the alternative formula. It is considered, therefore, that the brown solution contains one form of the anthranol corresponding with alizarin, and the precipitate obtained by acidifying the brown solution consists of the other form, the possible formulæ being $C_6H_4 \begin{smallmatrix} \text{C(OH)} \\ | \\ \text{CH} \end{smallmatrix} \text{---} C_6H_2(OH)_2$ and



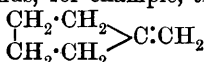
The isomeride of alizarinimide is also formed when the brown, olive-green, or yellow reduction products of alizarin, referred to in the first paragraph, are dissolved in ammonia solution and exposed to air.

Two anthrapurpurinimides were obtained from anthrapurpurin: these resembled the alizarinimides. Flavopurpurin also yields a similar substance when its corresponding anthranol is treated with ammonia solution.

T. A. H.

Preparation of Camphor from Borneol or *iso*Borneol. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 161306. Compare Abstr., 1905, i, 709; this vol., i, 28).—When borneol or *isoborneol* is dissolved in 95 per cent. acetic acid or light petroleum, water added, and a current of ozone passed through the solution at the ordinary temperature, camphor is formed readily. Camphene under similar conditions yields only camphenilone and formaldehyde. C. H. D.

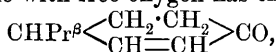
Terpenes and Ethereal Oils. LXXIII. OTTO WALLACH (*Annalen*, 1905, 343, 28—40. Compare Abstr., 1903, i, 103, 105, 567; 1904, i, 74, 104, 424, 752, 753, 754, 987, 1035; 1905, i, 147, 450, 709).—A special name is suggested for the methylene group, CH_2 , which is found in semicyclic linking in many hydroaromatic and analogous compounds and in the methylenequinone and other substances studied by Auwers and Zincke. Such a methylene group has characteristic reactions which distinguish it from the same group in cyclic or acyclic molecules. Semmler has suggested the name " ψ -terpenes" for terpenes possessing this semicyclic methylene group. But such hydrocarbons do not bear to the terpenes the relation which ψ -compounds in general bear to their isomerides. It is consequently suggested that the acyclic methylene group found in limonene, carvone, citronellal, and *isopulegone* should be called "methene." Thus, for example, the expression



represents methenecyclopentane (methenecyclopentamethylene), the expression $\begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \end{matrix} > \text{C} : \text{CH}_2$, methenecycloheptane; β -phellandrene, $\text{CHPr}^\beta < \begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH} = \text{CH} \end{matrix} > \text{C} : \text{CH}_2$, is called Δ^2 -1-methene-4-*isopropylcyclohexene* or 1-methene-4-*isopropyltetrahydrobenzene*.

Experiments have been made in order to determine whether the tetrahydrocuminaldehyde obtained by oxidation by β -phellandrene (Abstr., 1905, i, 709) is present in the source of the phellandrene (oil of *Phellandrium aquaticum*) or whether it is formed in the oxidation of the phellandrene in the process of preparation.

Phellandrene was shaken with an equal quantity of water in a large flask with oxygen at the ordinary temperature and exposed to sunlight. Oxygen is rapidly absorbed; when the absorption has ceased after three days, a heavy, viscous oil remains, which is distilled in steam; at first, unchanged phellandrene distils over, mixed with a small amount of a substance which yields a semicarbazone. The non-volatile product does not contain a glycol. The *semicarbazone*, $\text{C}_9\text{H}_{14} \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, melts at $183-184^\circ$ and is converted by oxalic or sulphuric acid into an unsaturated *ketone*, $\text{C}_9\text{H}_{14}\text{O}$, which boils at $103-106^\circ$ under 15 mm. or at $220-224^\circ$ under the ordinary pressure; it has a sp. gr. 0.9387 and n_D 1.4788 at 26° . The ketone combines easily with sodium hydrogen sulphite, but is unchanged when treated with sodium hypobromite, and yields with hydrogen sulphide in ammoniacal solution a sulphur compound which melts at $121-122^\circ$. When reduced with sodium in moist ether, an alcohol is formed in small quantity with an odour resembling that of terpineol; it is oxidised in acetic acid solution to a saturated *ketone*, $\text{C}_9\text{H}_{16}\text{O}$, the *semicarbazone* of which melts at 188° . The ketone is oxidised by chromic acid in sulphuric acid solution to β -*isopropyladipic acid*. Hence it follows that the product of oxidation of β -phellandrene with free oxygen has the constitution

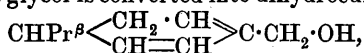


and is therefore 1-*isopropyl*- Δ^2 -*cyclohexene*-4-one. Further, the tetrahydrocuminaldehyde is an original constituent of the ethereal oils in which it is found, and not formed from the phellandrene. The conclusion may also be drawn from the experiments that the oxidation of an unsaturated compound by permanganate follows a different course from the oxidation of that compound by oxygen in the presence of water. The oxidation of the ethylene linking by oxygen is brought about by the addition of oxygen and the conversion of the double into the single linking, whilst the oxidation by permanganate brings about the addition of two hydroxyl groups at the ethylene linking. The reaction with oxygen is identical with that with ozone.

Attention is called to the fact that the odour of cyclic ketones depends on the relative positions of the carbonyl and the *isopropyl* group; thus, when they occupy *o*-positions relative to one another, the ketone has the odour of menthone, in the *m*-position relative to one another the odour of carvone, and in the *p*-position a cumin-like odour.

When β -phellandrene glycol, $\text{CHPr}^\beta < \begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH} = \text{CH} \end{matrix} > \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$, is

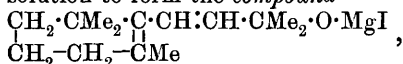
oxidised by chromic acid in sulphuric acid solution, 1-isopropylhexene-4-one is formed. The glycol is converted into dihydrocuminolalcohol,



together with tetrahydrocuminolaldehyde, on boiling with dilute sulphuric acid. When the aldoxime (m. p. 87°) of the tetrahydrocuminolaldehyde just mentioned is reduced in alcoholic solution with sodium, a base is obtained the carbamide of which melts at 160 — 161° and is identical with the base formed together with the carbamide of cuminylamine from nitro- β -phellandrene; the base, therefore, is probably a derivative of tetrahydrocuminylamine. These facts are in favour of the constitution of nitro- β -phellandrene previously suggested (Abstr., 1905, i, 709).

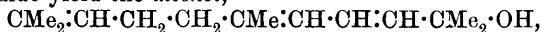
By the reactions above described, the question as to the occurrence of β -phellandrene together with the α -isomeride in the ethereal oil from *Eucalyptus amygdalina* has been decided; but a very small quantity of β -phellandrene is present. K. J. P. O.

Tertiary Alcohols of the cycloCitrylidene Series. ALBERT VERLEY (D.R.-P. 160834. Compare Abstr., 1904, i, 880).—Certain cyclic citral derivatives combine with magnesium alkyl iodides, and the resulting compounds are decomposed by water to form tertiary alcohols. Thus, methyl cyclocitrylideneacetate combines with magnesium methyl iodide in ethereal solution to form the compound



which is converted by water into cyclocitrylidene-tert.-butyl alcohol, $\text{C}_{14}\text{H}_{24}\text{O}$, which boils at 131° under 16 mm. pressure, has a sp. gr. 0.9003 at 15° , and has a fresh odour of violets. The same alcohol is obtained from ionone and magnesium methyl iodide. The corresponding alcohol, $\text{C}_{16}\text{H}_{28}\text{O}$, from ethyl cyclocitrylideneacetate and magnesium ethyl iodide, boils at 162° under 16 mm. pressure and has a sp. gr. 0.94229 at 15° . The alcohol, $\text{C}_{15}\text{H}_{26}\text{O}$, from ionone and magnesium ethyl iodide, boils at 153° under 15 mm. pressure.

The same series of tertiary alcohols may be obtained by combining the open chain esters of citrylideneacetic acid with magnesium alkyl iodides and converting the products into their cyclic isomerides by means of dilute acids. Thus, methyl citrylideneacetate and magnesium methyl iodide yield the alcohol,



which boils at 154° under 18 mm. pressure and has a sp. gr. 0.890 at 15° . C. H. D.

Action of Atmospheric Oxygen on Para Caoutchouc. EDGAR HERBST (Ber., 1906, 39, 523—525).—When a current of purified air is passed for 140 hours through a hot solution of Para caoutchouc in benzene, two substances are obtained: a transparent, reddish-brown syrup, soluble in light petroleum, having the composition $\text{C}_{10}\text{H}_{16}\text{O}$, and an amorphous, friable, yellow solid of the composition $\text{C}_{10}\text{H}_{16}\text{O}_3$, insoluble in light petroleum. The latter is sparingly soluble in a mixture of benzene and light petroleum; from this

solvent, a modification separates as a hard, glassy mass with substantially different physical properties. C. S.

Occurrence of β -Amyrin Acetate in some Varieties of Gutta-percha. PIETER VAN ROMBURGH and N. H. COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 544—546. Compare Romburgh, *Abstr.*, 1904, i, 905; this vol., i, 20).—The acetic ester obtained from the gutta-percha of *Payena Leerii* and from djelutung is identical with β -amyrin acetate (Vesterberg, *Abstr.*, 1891, 165); it melts at 240—241° (corr.) and has $[\alpha]_D + 81.1^\circ$ in chloroform solution. The β -amyrin obtained on hydrolysis of the acetate crystallises in long, thin needles, melts at 197—197.5° (corr.), and has $[\alpha]_D + 88^\circ$ in chloroform or $+ 98^\circ$ in benzene solution; when treated with benzoic chloride in pyridine solution, it forms the benzoate, which crystallises in small, rectangular plates and melts at 234—235° (corr.).

The substance melting at 239—240°, obtained by Marek from the milky juice of *Asclepius syriaca* (*Abstr.*, 1904, ii, 141), and α -balalban, obtained from balata by Tschirch and Schereschewski (*Abstr.*, 1905, i, 713), also are identical with β -amyrin acetate. G. Y.

Heerabol Myrrh. ALEXANDER TSCHIRCH and W. BERGMANN (*Arch. Pharm.*, 1906, **243**, 641—654).—The material examined was a commercial sample of *Myrrha electa*; it consisted of reddish-brown pieces with a waxy fracture, and the following solvents dissolved the percentages of it indicated: alcohol, 36; ether, 29; chloroform, 31; light petroleum, 9; methyl alcohol, 38; water, 60; ethyl and methyl alcohols, 36; toluene, 30.

From an ethereal extract of the drug, ammonium carbonate and sodium carbonate alike dissolved nothing. One per cent. aqueous potassium hydroxide, however, dissolved the following two amorphous, greyish-yellow, neutral substances, which were separated in alcoholic solution by means of lead acetate, with which the first of them forms an insoluble precipitate, but not the second: α -heerabo-myrrhol, $C_{17}H_{24}O_5$, melting at 158—165°, and β -heerabo-myrrhol, $C_{19}H_{28}O_4$, melting at 116—124°.

From the residue insoluble in ether, alcohol extracted two brown, amorphous substances, soluble in dilute aqueous potassium hydroxide: α -heerabo-myrrholol, $C_{15}H_{22}O_7$ or $C_{30}H_{44}O_{14}$, melting at 207—220°, and β -heerabo-myrrholol, $C_{29}H_{36}O_{10}$, melting at 205—213°; of these, the first is precipitated from the solution by lead acetate, the second is not.

From the ethereal solution, after the extraction with alkali, the ether was driven off and the residue distilled with steam; an essential oil passed over. More of this oil was obtained by repeated distillation of the residue with very dilute aqueous potassium hydroxide; at the same time, a substance dissolved gradually in the alkali which melted at 188—197° and had the composition and reactions of α -heerabo-myrrhol. The *heeraboresen* finally remaining, $C_{29}H_{40}O_4$, melted at 98—104°. The *essential oil* was yellow, rather syrupy, and had the sp. gr. 1.046; it resinified readily.

The unusually high percentage of oxygen in these substances is noteworthy.

From the residue remaining after extraction with ether and alcohol, water extracted a mixture of a *gum* with an *enzyme* having the character of an oxydase. This mixture could not be separated into its constituents; it yielded 5.15 per cent. of ash containing calcium and magnesium, and gave pyrrole when heated with dry potassium hydroxide, furfuraldehyde when distilled with 12 per cent. hydrochloric acid, mucic acid when treated with nitric acid, and arabinose when hydrolysed with 5 per cent. sulphuric acid.

The *bitter principle* was not isolated in a state of purity.

The sample contained in 100 parts, approximately: heerabo-myrrhol, α , 4 (and secondary 2), β , 2; heerabo-myrrholol, α , 3, β , 2; heeraboresen, 6; essential oil, 6—7 (and secondary 1.5); gum and enzyme, 61; impurities, 3—4; water, 5.

Two small specimens collected from unknown species of *Commiphora* in German East Africa were also examined cursorily. C. F. B.

***d*-Glucosephloroglucinol and β -Glucosan.** EDUARD VONGERICHTEN and FR. MÜLLER (*Ber.*, 1906, **39**, 241—245).—When *d*-glucose-apigenin is boiled for five hours with a 25 per cent. solution of sodium hydroxide, it yields *d*-glucosephloroglucinol, which is in its turn partially converted into phloroglucinol and β -glucosan. From an aqueous solution containing *d*-glucosephloroglucinol and β -glucosan, the former is precipitated by the addition of lead acetate. *d*-Glucosephloroglucinol is a white, amorphous, hygroscopic powder dissolving readily in alcohol. In aqueous solution it has $[\alpha]_D - 24.20^\circ$ at 20° , in alcoholic solution, $[\alpha]_D - 24.95^\circ$ at 20° . It is unaffected by yeast or emulsin and reduces Fehling's solution only after having been boiled with mineral acids. It reacts with diazonium salts to form disazo-compounds: *d*-glucosephloroglucinoldisazochlorobenzene, $C_{24}H_{22}O_8N_4Cl_2$, is a reddish-brown, flocculent precipitate obtained from *p*-chlorophenyl-diazonium chloride; *d*-glucosephloroglucinoldisazobenzene, $C_{24}H_{24}O_8N_4$, obtained from diazobenzene chloride, forms a reddish-brown, crystalline mass, soluble in alkalis.

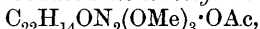
β -Glucosan, obtained as described above, forms large, rhombic plates melting at 177 — 178° and is identical with Tanret's lævoglucosan (*Abstr.*, 1894, i, 564).

The tribenzoyl derivative, in contradistinction to the triacetyl compound, is scarcely hydrolysed by hydrochloric acid. A boiling solution of baryta-water changes β -glucosan into a *hydrate*, which melts at 108° and in a vacuum loses water, re-forming β -glucosan. β -Glucosan is almost unaffected by bromine or potassium permanganate in neutral solution, but is converted into dextrose by hydrochloric acid. C. S.

Brazilin and Hæmatoxylin. JOSEF HERZIG and JACQUES POLLAK (*Ber.*, 1906, **39**, 265—267. Compare *Abstr.*, 1903, i, 270, 713; 1904, i, 81; 1905, i, 605).—On warming on the water-bath a solution of tetramethylhæmatoxylone in glacial acetic acid with phenylhydrazine, a compound, $C_{22}H_{12}ON_2(OMe)_4$, is obtained, analogous with the substance prepared in a similar manner from trimethylbrazilone; it crystallises from ethyl acetate in yellow needles, melts at 234 — 237° ,

and is not affected by acetic anhydride or an excess of phenylhydrazine.

The phenylhydrazine derivative of trimethylbrazilone (*loc. cit.*) cannot be directly acetylated, but when heated with acetic anhydride, sodium acetate, and zinc dust, a reduced *monoacetyl* derivative,



is obtained; this crystallises from alcohol, melts at 214—217°, and when hydrolysed gives a product which is oxidised by ferric chloride to the original phenylhydrazine derivative melting at 240—243°.

The bearing of these facts on the structure of brazilin is discussed.

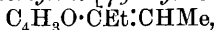
W. A. D.

Grignard Syntheses in the Furan Group. WILLIAM J. HALE, W. D. McNALLY, and C. J. PATER (*Amer. Chem. J.*, 1906, 35, 68—78).

—*Diphenyl-2-furylecarbinol*, $\begin{array}{c} \text{CH}\cdot\text{CH} \\ | \quad \diagup \\ \text{CH}-\text{O} \end{array} \text{CPh}_2\cdot\text{OH}$, obtained by treating

ethyl pyromucate with magnesium phenyl bromide and decomposing the product with water, crystallises in colourless, rhombic prisms, melts at 92.4° (corr.), is soluble in ether, alcohol, chloroform, benzene, ethyl acetate, or warm light petroleum, and gradually changes into a dark red, gummy mass; its *methyl ether* is a colourless oil which boils at 206—207° under 26 mm. pressure and has a sp. gr. 1.1195 at 20°.

2-*Furyldiethylcarbinol*, $\begin{array}{c} \text{CH}\cdot\text{CH} \\ | \quad \diagup \\ \text{CH}-\text{O} \end{array} \text{CEt}\cdot\text{OH}$, was obtained as a pale yellow liquid which had a pleasant, ethereal odour and gradually changed into a dark brown, crystalline mass; it could not be purified by distillation, as it readily suffers decomposition with formation of β -2-furyl- α -methyl- β -ethylethylene [γ -furyl- Δ^{β} -amylene],



which crystallises in colourless needles or prisms, melts at 249° (corr.), is soluble in chloroform, benzene, carbon disulphide, ether, or light petroleum, is insoluble in water, and decolorises a solution of bromine in carbon disulphide.

By the action of magnesium methyl iodide on ethyl pyromucate, an unstable, red liquid is produced.

Dibenzyl-2-furylecarbinol, $\text{C}_4\text{OH}_3\cdot\text{C}(\text{C}_7\text{H}_7)_2\cdot\text{OH}$, crystallises in silky needles, melts at 82.7° (corr.), is soluble in the usual organic solvents and insoluble in water, and is much more stable than the corresponding diphenyl derivative; its *methyl ether* crystallises in long, colourless needles and melts at 61.2° (corr.).

Furylene-2:5-bisdiphenylecarbinol, $\text{C}_4\text{OH}_2(\text{CPh}_2\cdot\text{OH})_2$, obtained by the action of magnesium phenyl bromide on ethyl dehydromucate, forms small, colourless, rhombic crystals, melts at 165.5° (corr.), is soluble in alcohol, ether, acetone, benzene, or chloroform, and is more stable than diphenyl-2-furylecarbinol; its *methyl ether* crystallises in groups of white needles and melts at 88.2° (corr.); the *ethyl ether* forms rhombic prisms and melts at 171° (corr.).

Furylene-2:5-bisdibenzylecarbinol, $\text{C}_4\text{OH}_2[\text{C}(\text{C}_7\text{H}_7)_2\cdot\text{OH}]_2$, is a fairly stable substance of a light straw colour; it boils and partially decomposes at 193—195° under 30 mm. pressure, has an agreeable odour, a

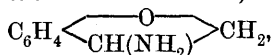
sp. gr. 1.126 at 27°, and is soluble in all the usual solvents except light petroleum and water. E. G.

1- and 2-Aminocoumaran (Coumaranamine). RICHARD STOERMER and W. KÖNIG (*Ber.*, 1906, 39, 492—499. Compare Stoermer and Calov, *Abstr.*, 1901, i, 336).—Hydrocoumarilic acid (coumaranilic acid), prepared by the reduction of coumarilic acid in alkaline solution by sodium amalgam, melts at 116.5°; its ethyl ester boils at 273° and melts at 23°. *Coumaranilic hydrazide*, prepared from ethyl coumaranilate and hydrazine hydrate, separates from alcohol in snow-white needles and melts at 148°. *Dicoumaranilic hydrazide*, $C_8H_7O \cdot CO \cdot NH \cdot NH \cdot CO \cdot C_8H_7O$, crystallises in needles. *Coumaranilic azoimide*, $N_3 \cdot CO \cdot C_8H_7O$, prepared by dissolving coumaranilic hydrazide in water and gradually adding sodium nitrite (2 mols.) and dilute acetic acid, is a snow-white solid and melts at 32°. It is probably formed as an intermediate product in the preparation of dicoumaranilic hydrazide from coumaranilic hydrazide; thus

$C_8H_7O \cdot CO \cdot NH \cdot NH_2 + N_3 \cdot CO \cdot C_8H_7O = N_2H_2(CO \cdot C_8H_7O)_2 + HN_3$ represents the formation of dicoumaranilic hydrazide. When coumaranilic azoimide is heated with absolute alcohol, 1-carboxyethylaminocoumaran (1-urethylcoumaran), $C_8H_7O \cdot NH \cdot CO_2Et$, melting at 105°, is formed. *Phenylurethylcoumaran*, prepared from coumaranilic azoimide and phenol, forms glistening leaflets and melts at 151°. *Dicoumaranyl carbamide*, $CO(NH \cdot C_8H_7O)_2$, prepared by boiling the azoimide with water, separates from dilute alcohol as a crystalline powder and melts at 205°. *Coumaranilic anilide*, prepared by the action of aniline on the azoimide, separates from dilute alcohol in glistening scales and melts at 104°.

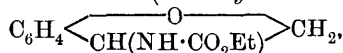
Coumarone was formed as one of the products of the action of cold concentrated hydrochloric acid on coumaranyluethane.

Coumaranone was prepared by the dehydration of phenoxyacetic acid with phosphoric oxide (compare Stoermer and Bartsch, *Abstr.*, 1901, i, 94). Its oxime, when reduced by sodium amalgam and glacial acetic acid, yielded 2-aminocoumaran,



as a yellow oil which boils at 122° under 18 mm. pressure. It has the sp. gr. 1.1303 at 17° and n_D 1.5645 at 19°. Its *hydrochloride* melts and decomposes at 226°; its *platinichloride* decomposes at 220°; its *aurichloride* melts and decomposes at 161°.

2-Carboxyethylaminocoumaran (2-urethylcoumaran),



prepared from 2-aminocoumaran and ethyl chlorocarbonate, separates from dilute alcohol in needles and melts at 101.5°.

Coumaranylphenylcarbamide, $C_6H_4 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}(\text{NH} \cdot \text{CO} \cdot \text{NHPh}) \end{array} \text{CH}_2,$

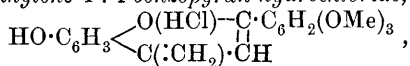
prepared from 2-aminocoumaran and phenylcarbimide, separates from dilute alcohol in needles and melts at 204°.

Coumarone and ammonium chloride are formed when 2-aminocoumaran hydrochloride is heated.

2-Coumaranol nitrite, $\text{C}_6\text{H}_4 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}(\text{O}\cdot\text{NO}) \end{array} \text{CH}_2$, prepared from 2-aminocoumarone hydrochloride and potassium nitrite, separates from dilute alcohol in glistening leaflets and melts at 65° . When heated, it decomposes into coumarone and nitrous acid. A. McK.

7-Hydroxy-2-o-m-p-trimethoxyphenyl-4-methylene-1:4-benzopyran and its Derivatives. CARL BÜLOW and CARL SCHMID (*Ber.*, 1906, 39, 214—225. Compare Abstr., 1901, i, 400, 559; 1904, i, 262; 1905, i, 150).—The copper derivative of 2:3:4-trimethoxybenzoylacetone (Blumberg and Kostanecki, Abstr., 1903, i, 644) separates from dilute alcohol in clusters of needles and melts at 150 — 152° .

Resorcinol condenses with 2:3:4-trimethoxybenzoylacetone in the presence of dry hydrogen chloride to form 7-hydroxy-2-o-m-p-trimethoxyphenyl-4-methylene-1:4-benzopyran hydrochloride,



which is obtained in clusters of dark yellow needles soluble in water or alcohol. A concentrated aqueous solution is orange-yellow in colour, turning red on dilution owing to hydrolytic dissociation. The sulphate forms tufts of silky needles which melt at 203° to a steel-blue liquid. The picrate, $\text{C}_{25}\text{H}_{21}\text{O}_{12}\text{N}_3$, forms minute, yellow needles which darken at 100° , become black at 200° , and melt and decompose at 212° . The free base, obtained from an aqueous solution of the hydrochloride by adding a slight excess of ammonium hydroxide and then neutralising with acetic acid, separates in light red, microcrystalline flocks, sinters at 95° , becomes dark and melts at 105 — 110° . The acetyl derivative, $\text{C}_{21}\text{H}_{20}\text{O}_6$, melts at 245 — 247° .

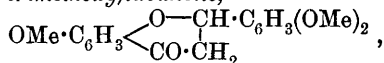
By reduction with zinc dust and acetic acid in the presence of acetic anhydride, the base yields a dihydro-derivative, $\text{C}_{21}\text{H}_{22}\text{O}_6$, which forms a greenish-yellow, amorphous powder and melts at 230 — 235° .

By brominating the hydrochloride in acetic acid, a dibromo-derivative is obtained, the hydrobromide of which, $\text{C}_{19}\text{H}_{18}\text{O}_5\text{Br}_2\cdot\text{HBr}$, forms red, prismatic crystals which blacken on heating, but do not melt below 270° . The base, $\text{C}_{19}\text{H}_{18}\text{O}_5\text{Br}_2$, forms small, greenish-brown needles which melt and decompose at 215° . Bromination of the hydrochloride in the presence of anhydrous sodium acetate leads to the formation of a tetrabromo-derivative, $\text{C}_{19}\text{H}_{18}\text{O}_5\text{Br}_4$, which crystallises in dark red prisms and does not melt below 300° .

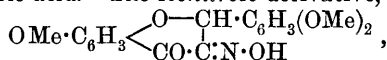
7-Hydroxy-2-o-m-p-trihydroxyphenyl-4-methylene-1:4-benzopyran hydrochloride, $\text{C}_{16}\text{H}_{12}\text{O}_5\cdot\text{HCl}$, is obtained by heating the corresponding trimethoxy-compound at 150 — 180° with hydrochloric acid. It crystallises in small, red leaflets with blue reflex, and in solution is more stable than the hydrochloride of the trimethyl ether. The base, $\text{C}_{16}\text{H}_{12}\text{O}_5$, crystallises in minute, brown needles which partially decompose on exposure to air. Concentrated sulphuric acid dissolves it, forming an orange-red, non-fluorescent solution. C. S.

Synthesis of 6:2':4'-Trihydroxyflavonol. E. BONIFAZI, STANISLAUS VON KOSTANECKI, and JOSEF TAMBOR (*Ber.*, 1906, 39, 86—91).—2:4-Dimethoxybenzaldehyde and quinacetophenone mono-

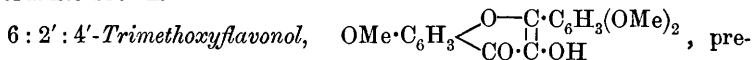
methyl ether (Abstr., 1904, i, 440) condense in warm alcoholic sodium hydroxide solution, forming 2'-hydroxy-5':2:4-trimethoxychalkone, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_3(\text{OMe})_2$, which crystallises in slender, orange needles, melts at 118° , and gives a red coloration with concentrated sulphuric acid. When heated with acetic anhydride and sodium acetate, it yields 2'-acetoxy-5':2:4-trimethoxychalkone, $\text{C}_{15}\text{H}_8\text{O}_2(\text{OMe})_3\cdot\text{OAc}$, which crystallises in yellow needles and melts at 87° , and 6:2':4'-trimethoxyflavanone,



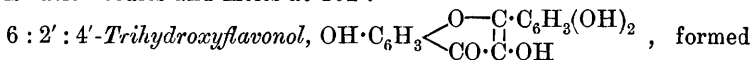
which is formed also by boiling 2'-hydroxy-5':2:4-trimethoxychalkone with alcoholic hydrochloric acid in a reflux apparatus. It crystallises in yellow prisms, melts at 160° , and gives a red coloration with concentrated sulphuric acid. The isonitroso-derivative,



formed by the action of amyl nitrite and hydrochloric acid on the preceding compound in alcoholic solution, crystallises in small, yellow needles, melts and decomposes at $173-175^\circ$, dissolves in aqueous sodium hydroxide to form a yellow solution, and dyes with cobalt mordants orange, uranium, cadmium, and lead mordants yellow, and copper mordants brown.

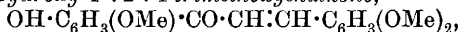


pared by boiling the isonitroso-compound with sulphuric acid in glacial acetic acid solution, crystallises in yellow spears, melts at 193° , when warmed with dilute sodium hydroxide forms a sparingly soluble yellow sodium derivative, dyes with alumina mordants a light yellow, and dissolves in concentrated sulphuric acid to form a greenish-yellow solution which becomes almost colourless and shows a green fluorescence. The acetyl derivative crystallises from dilute alcohol in prismatic needles and melts at 162° .



by boiling the trimethoxy-compound with concentrated hydriodic acid, crystallises in light yellow needles containing H_2O , which is lost at 130° , melts at 285° , and dissolves in dilute sodium hydroxide to form a greenish-yellow solution with strong green fluorescence, in concentrated sulphuric acid to form a yellow solution with slight green fluorescence. It dyes fibres mordanted with alumina yellow, with iron salts, olive-brown to almost black. When boiled with acetic anhydride and sodium acetate, it forms the tetra-acetyl derivative, $\text{C}_{15}\text{H}_6\text{O}_2(\text{OAc})_4$, which crystallises from dilute alcohol in white needles and melts at 163° . G. Y.

Dyeing Properties of 7:2':4'-Trihydroxyflavonol. STANISLAUS VON KOSTANECKI, VICTOR LAMPE, and S. TRIULZI (*Ber.*, 1906, 39, 92-96).—2'-Hydroxy-4':2:4-trimethoxychalkone,



is obtained in the form of its yellow sodium derivative by the con-

densation of 2:4-dimethoxybenzaldehyde with resacetophenone monomethyl ether (pæonol) in hot alcoholic sodium hydroxide solution; when liberated by means of hydrochloric acid and recrystallised from alcohol, the chalkone forms yellow needles, melts at 157° , and gives a red coloration with concentrated sulphuric acid. 2'-Acetoxy-4':2:4-trimethoxychalkone, $C_{15}H_{16}O_2(OMe)_3 \cdot OAc$, crystallises from dilute alcohol in yellow, nodular aggregates and melts at $110-112^{\circ}$. When boiled with alcoholic hydrochloric acid in a reflux apparatus for twenty-four hours, the chalkone is partially converted into 7:2':4'-trimethoxyflavanone, $OMe \cdot C_6H_3 \begin{smallmatrix} O-CH \cdot C_6H_3(OMe)_2 \\ | \\ CO \cdot CH_2 \end{smallmatrix}$, which is extracted from

the mixture by much boiling water; it crystallises from dilute alcohol in white needles, melts at 139° , and dissolves in alcoholic sodium hydroxide to a yellow, in concentrated sulphuric acid to a red, solution.

The isonitroso-derivative, $OMe \cdot C_6H_3 \begin{smallmatrix} O-CH \cdot C_6H_3(OMe)_2 \\ | \\ CO \cdot C \cdot N \cdot OH \end{smallmatrix}$, forms small, yellow crystals, melts and decomposes at 172° , dissolves in dilute sodium hydroxide to form a yellow solution, and dyes with cobalt mordants yellow.

7:2':4'-Trimethoxyflavonol, $OMe \cdot C_6H_3 \begin{smallmatrix} O-C \cdot C_6H_3(OMe)_2 \\ | \\ CO \cdot C \cdot OH \end{smallmatrix}$, crystallises from alcohol in yellow spears, melts at 205° , and dyes with aluminium mordants a light yellow; when warmed with aqueous sodium hydroxide, it forms a sparingly soluble, yellow sodium derivative, and dissolves in concentrated sulphuric acid to form a yellow solution with an intense bluish-green fluorescence. The acetyl derivative,

$C_{15}H_{16}O_2(OMe)_3 \cdot OAc$, crystallises from dilute alcohol in short prisms and melts at $189-191^{\circ}$.

7:2':4'-Trihydroxyflavonol (resomorin), formed by boiling 7:2':4'-trimethoxyflavonol with concentrated hydriodic acid, separates from dilute alcohol as a gelatinous mass; its behaviour towards metallic mordants is the same as that of 6:2':4'-trihydroxyflavonol (see preceding abstract) and of morin. The character of the last-named substance as a dye must depend therefore on the presence of the group $-CO \cdot C(OH)-$, and not on the presence of a hydroxyl in the *peri*-position to the carbonyl group. When boiled with acetic anhydride and sodium acetate, resomorin forms the tetra-acetyl derivative,

$OAc \cdot C_6H_3 \begin{smallmatrix} O-C \cdot C_6H_3(OAc)_2 \\ | \\ CO \cdot C \cdot OAc \end{smallmatrix}$, which crystallises in rosettes of small, stout needles and melts at $129-130^{\circ}$. G. Y.

Cotarnine Ferrichloride. ARNOLD VOSWINKEL (D.R.-P. 161400).—On mixing solutions of ferric chloride and cotarnine hydrochloride in absolute alcohol, cotarnine ferrichloride, $C_{12}H_{13}O_3N \cdot HFeCl_4$, is precipitated in orange leaflets, slowly agglomerating to form ruby-red crystals. The same compound is obtained on heating anhydrous ferric chloride with cotarnine hydrochloride in a vacuum. The salt dissolves in water or dilute alcohol and is decomposed on boiling. It finds therapeutic application as a styptic. C. H. D.

Transformation of α -Methylmorphimethine into the β -Compound by Heat. Crystallographic Behaviour of the Two Isomerides. ROBERT PSCHORR, HEINRICH ROTH, and F. TANNHÄUSER (*Ber.*, 1906, **39**, 19—26).—When α -methylmorphimethine is heated in a vacuum, it changes to a violet liquid, which then assumes a clear yellow colour; if the temperature is then suddenly raised, a yellow oil distils at 220—240° under 12 mm. pressure, consisting of the β -isomeride previously prepared by the action of alcoholic potash (Knorr and Smiles, *Abstr.*, 1902, i, 817); its identity was confirmed by preparing the benzoate and the methiodide.

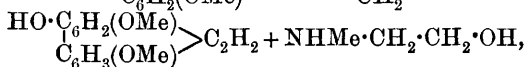
α -Methylmorphimethine separates from dilute alcohol in crystals belonging to the sphenoidal-rhombic system [$a : b : c = 0.7265 : 1 : 0.5142$], which exhibit rotatory polarisation in the solid state as well as in solution. The β -isomeride crystallises in the same system [$a : b : c = 0.5832 : 1 : 0.9560$].

α -Ethylthiocodide also crystallises in the same system [$a : b : c = 0.7481 : 1 : 0.7659$]. T. M. L.

Resolution of Thebaine by Benzoyl Chloride. ROBERT PSCHORR and W. HAAS (*Ber.*, 1906, **39**, 16—19).—*Benzoylthebaol*, $C_{23}H_{18}O_4$, prepared by the action of benzoyl chloride on thebaine at 0°, crystallises from acetic acid in thin, colourless needles and melts at 160—161°. The *dibromo-derivative*, $C_{23}H_{16}O_4Br_2$, crystallises from acetic acid in long needles and melts at 229°.

Benzoylthebaolquinone, $C_{23}H_{16}O_6$, prepared by oxidation with chromic acid, separates from acetic acid in yellow crystals and melts at 216°; it is hydrolysed by sodium ethoxide to Freund's thebaolquinone.

The basic product of the action of benzoyl chloride was identified by means of its aurichloride, $C_3H_{10}ONaAuCl_4$, as ethoxymethylamine. The decomposition is thus essentially similar to that brought about by acetic anhydride, $O \begin{array}{c} \diagup C_6H_2(OMe) \\ \diagdown C_6H_2(OMe) \end{array} > C_2H_2 \begin{array}{c} \diagup NMe \\ \diagdown CH_2 \end{array} > CH_2 \rightarrow$

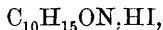


and involves the resolution of a furan ring and of a nitrogen ring and the separation of a carbon to carbon linking. T. M. L.

Hordenine: a New Alkaloid obtained from Malt Germs. EUGÈNE LÉGER (*Compt. rend.*, 1906, **142**, 108—110).—*Hordenine*, $C_{10}H_{15}ON$, a new alkaloid extracted by Stas' method from malt germs, forms colourless, voluminous, strongly doubly refracting orthorhombic prisms [$a : b : c = 0.5257 : 1 : 0.3551$ (Wyruboff)]. It melts at 117.8° (corr.), sublimes like camphor at 140—150°, dissolves readily in alcohol, chloroform, or ether, forming optically inactive solutions, is sparingly soluble in benzene, and is almost insoluble in toluene, xylene, or light petroleum.

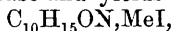
Hordenine is alkaline towards litmus or phenolphthalein, liberates ammonia from its salts, and is not attacked by concentrated sulphuric acid or by potassium hydroxide, either fused or in aqueous solution. It reduces acid solutions of potassium permanganate, ammoniacal solu-

tions of silver nitrate or iodic acid, and forms soluble salts with acids; the *sulphate*, $(C_{10}H_{15}ON)_2 \cdot H_2SO_4 \cdot H_2O$, crystallises in brilliant, prismatic needles, readily soluble in water, sparingly so in alcohol; the *hydrochloride*, $C_{10}H_{15}ON \cdot HCl$, crystallises from alcohol in thin needles; the *hydrobromide*, $C_{10}H_{15}ON \cdot HBr$, forms brilliant, long, prismatic needles, readily soluble in water, less so in alcohol; the *hydriodide*,



crystallises in long prisms slightly less soluble than the preceding salt.

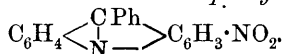
Hordenine is a tertiary base and yields a *methiodide*,



which crystallises from water in colourless prisms; it contains a phenolic hydroxyl group and reacts with acetic anhydride to form a syrupy *acetyl* derivative, which is basic and forms *acetylhordenine hydriodide*, $C_{10}H_{14}ONAc \cdot HI$, crystallising from alcohol or water in yellowish-white, tabular crystals.

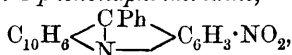
M. A. W.

New Synthesis of Phenylacridine Derivatives. FRITZ ULLMANN and HANS W. ERNST (*Ber.*, 1906, **36**, 298—310).—5-Nitro-2-anilinobenzophenone, $NHPh \cdot C_6H_3(NO_2) \cdot CPh$, prepared by heating aniline with 2-chloro-5-nitrobenzophenone and potassium carbonate for three hours at 180° , crystallises from alcohol, melts at 155° , and by heating with glacial acetic acid containing a little concentrated sulphuric acid is converted into 3-nitro-5-phenylacridine,



This can also be prepared directly from 2-chloro-5-nitrobenzophenone by heating the latter with aniline and sodium acetate at 150° ; it crystallises from alcohol in intensely yellow needles and melts at 209° . On reduction, 3-amino-5-phenylacridine is obtained; Hess and Bernthsen (*Abstr.*, 1885, 800) describe this substance and its salts as resinous in character, but by the authors' method the *base* is obtained on crystallising from alcohol in the form of slender, yellow needles which melt at 200° ; the *hydrochloride* crystallises in large needles with a bronze-like lustre and in alcoholic solution shows a green fluorescence. 3-Acetyl-amino-5-phenylacridine crystallises from benzene, melts at 256° , and also shows a green fluorescence in alcoholic solution.

9-Nitro-7-phenyl-1 : 2-phenonaphthacridine,

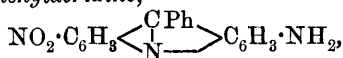


prepared by heating together 2-chloro-5-nitrobenzophenone and β -naphthylamine in nitrobenzene solution at 205° , crystallises from glacial acetic acid in straw-coloured needles, melts at 274° , and on reduction gives 9-amino-7-phenyl-1 : 2-phenonaphthacridine; this crystallises from alcohol in dark yellow prisms, melts at 282° , and gives a *hydrochloride* crystallising in red needles, which become yellow when heated with water.

9-Nitro-7-phenyl-2 : 1-phenonaphthacridine, prepared by heating 2-chloro-5-nitrobenzophenone with alcoholic α -naphthylamine for five hours at 150 — 170° , crystallises from glacial acetic acid in yellow needles and melts at 264° .

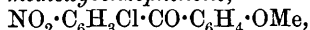
9-Amino-7-phenyl-2 : 1-phenonaphthacridine, crystallises from alcohol in stellate aggregates of brown needles, melts at 224°, and gives a red hydrochloride.

3-Nitro-7-amino-5-phenylacridine,

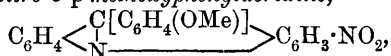


prepared by heating 2-chloro-5-nitrobenzophenone with *p*-phenylenediamine for three-quarters of an hour at 200°, crystallises from benzene in garnet-coloured needles and melts at about 181°; the hydrochloride forms yellowish-brown needles. On reduction, 3 : 7-diamino-5-phenylacridine is obtained, which crystallises from benzene in lemon-yellow needles; the picrate, $\text{C}_{19}\text{H}_{15}\text{N}_3 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, forms purplish-red needles.

2-Chloro-5-nitro-4'-methoxybenzophenone,

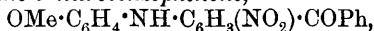


prepared from 2-chloro-4-nitrobenzoyl chloride and anisole by the Friedel-Crafts reaction, crystallises from benzene on adding light petroleum in colourless needles and melts at 105°. On heating it with aniline and powdered potassium carbonate at 180°, 5-nitro-2-anilino-4'-methoxybenzophenone, $\text{NHPh} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, is obtained; it crystallises from alcohol in yellow needles or plates, melts at 144–155°, and when heated with glacial acetic acid containing sulphuric acid is converted into 3-nitro-5-*p*-methoxyphenylacridine,



which crystallises from alcohol and melts at 178°.

2-o-Methoxyanilino-5-nitrobenzophenone,



prepared by heating 2-chloro-5-nitrobenzophenone with *o*-anisidine and potassium carbonate at 215°, crystallises from alcohol either in bright yellow needles sparingly soluble in the solvent or more soluble greenish-yellow leaflets; the two forms melt at 139° and are interconvertible.

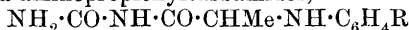
3-Nitro-9-methoxy-5-phenylacridine, prepared by heating together the same substances in the absence of potassium carbonate or by heating 5-nitro-2-*o*-methoxyanilinobenzophenone with concentrated sulphuric acid, crystallises from alcohol in orange-yellow needles and melts at 285°.

W. A. D.

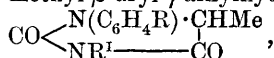
Nature of Oxazine and Thiazine Dyes. ARTHUR HANTZSCH (*Ber.*, 1906, 39, 153–159. Compare *Abstr.*, 1905, i, 605).—Largely polemical in reply to Kehrmann (*ibid.*, i, 670). The ammonium quinonoid constitutional formulæ are regarded as being more in harmony with known facts than are Kehrmann's oxonium or thiazonium formulæ. Bernthsen's methylene-azure (O. Fischer, *Ber.*, 1905, 38, 3435) has been examined, and in solution its salts behave as neutral salts and are comparable with the aromatic quaternary ammonium salts. The azure-blue colour of the solution persists for a long time after the addition of sodium acetate or carbonate. This would not be probable if the compound contained the group $\geq \text{SO} \cdot \text{Cl}$.

J. J. S.

Arylhydantoin. GUSTAV FRERICHs and M. HOLLMANN (*Arch. Pharm.*, 1905, **243**, 684—710. Compare Abstr., 1899, i, 806; 1903, i, 16).—Substituted aminopropionylcarbamides,



[R = H or Me], were prepared by heating α -bromopropionylcarbamide, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CHMeBr}$ (H. Frerichs, *Arch. Pharm.*, 1903, **241**, 195), with an arylamine, $\text{NH}_2 \cdot \text{C}_6\text{H}_4\text{R}$, in alcoholic solution. By heating the same mixture, without the addition of alcohol, to a higher temperature, or by heating the products just mentioned above their melting points, substituted α -methyl- β -arylhydantoins were prepared, and by heating these with alkyl iodides, R^1I , and alcoholic potassium hydroxide, α -methyl- β -aryl- γ -alkylhydantoins,



were obtained (the allyl derivatives united with hydrogen bromide or bromine in acetic acid solution, forming bromo- and dibromo-propyl derivatives). Similar condensations took place with chloroacetic acid and with chloroacetamide; with ethylene bromide, 2 molecules of the hydantoins condensed. α -Methyl- β -phenylhydantoin was prepared not only by the method given above, but also by heating with alcoholic potassium hydroxide, α -bromopropionylphenylcarbamide, melting at 158° , which was obtained by mixing α -bromopropionyl bromide with phenylcarbamide in ethereal solution.

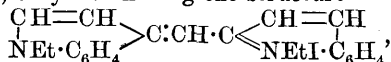
The other new substances described are enumerated below; the numbers indicate melting points.

Propionylcarbamides. α -Anilino-, 143° ; α -toluidino-, o 160° , m 156° , p 160° .

α -Methylhydantoins. β -Phenyl-, 146° ; β -tolyl-, o 167° , m 137° , p 173° . Derivatives of these in this order: γ -methyl-, 128° , 114° , 89° , 96° ; γ -ethyl-, 114° , liquid, 76° , 86° ; γ -allyl-, 88° , liquid, 58° , 96° ; γ -bromopropyl-, 89° liquid, 92° , 85° ; γ -dibromopropyl-, 137° (monobromo-substitution derivative of this, 148° ; obtained by the action of bromine in acetic acid solution), 104° , 85° , 101° ; γ -acetic acid-, 163° , 182° , 148° , 179° (barium salts crystallise with 3, 3, 2, $2\text{H}_2\text{O}$); γ -acetamide-, 225° , 166° , 159° , 205° ; γ -ethylene (di-), 200° , liquid, liquid, 173° .

C. F. B.

Constitution of the Cyanine Dyes. W. KÖNIG (*J. pr. Chem.*, 1906, [ii], **73**, 100—108. Compare Miethe and Book, Abstr., 1904, i, 622, 776; Book, this vol., i, 42).—As no case is known where a methyl group in the 2- or 3-position in pyridine or quinoline retains its property of condensing with aldehydes and ketones when the ring is reduced wholly or partially, it is probable that the cyanine dyes contain 2 atoms of hydrogen less than shown in Miethe and Book's formula (*loc. cit.*), ethyl-red having the structure

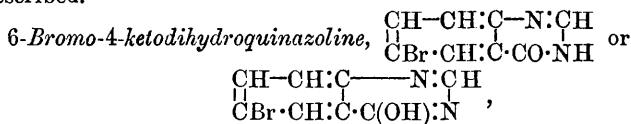


and the blue diethylcyanine, $\begin{array}{c} \text{CH}=\text{CH} \\ | \\ \text{NEt} \cdot \text{C}_6\text{H}_4 \end{array} > \text{C} : \text{CH} \cdot \text{C} \begin{array}{c} \text{CH}=\text{CH} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{NEtI} \end{array}.$

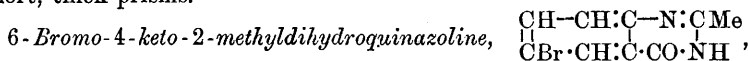
These formulæ are used to explain the similarity of the cyanine dyes

and the pyridine dyes obtained from furfuraldehyde (König, this vol., i, 109). Contrary to the view of Miethe and Book (*loc. cit.*), the additive compounds with iodine are considered to be periodides, as they are not lighter in colour than the parent dyes, as would be the case if the addition took place to an ethylene linking. G. Y.

Preparation of 6-Bromo-4-ketodihydroquinazolines from 5-Bromo-2-aminobenzoic Acid and certain of its Derivatives. MARSTON T. BOGERT and WILLIAM F. HAND (*J. Amer. Chem. Soc.*, 1906, 28, 94—104. Compare Abstr., 1904, i, 108).—Quinazolines have been prepared by the following methods. I. From 5-bromo-2-aminobenzoic acid: (1) by heating the acid with an acid anhydride or a nitrile in a sealed tube at 230—250°; this method gives a poor yield and an impure product; (2) by heating the acid or its ammonium salt with acid amides, a method which gives excellent results with formamide, but less satisfactory results with acetamide, and is not applicable to the higher amides; (3) by heating the acid with excess of glacial formic acid or an acid anhydride and afterwards adding excess of ammonium carbonate and continuing the heating; good yields are generally obtained in this way, and the products can be easily purified. II. By heating ammonium 5-bromo-2-acetylaminobenzoate, when a nearly quantitative yield is obtained. III. From 5-bromo-2-acetylaminobenzonitrile: (1) by warming it with solution of alkali dioxide; this method gives a quantitative yield of the pure substance; (2) by boiling it with concentrated hydrochloric acid. IV. By the action of primary amines on 5-bromo-2-acetylthranil. The following quinazolines are described.



crystallises in transparent, six-sided prisms, melts at 272—273° (corr.), and is soluble in alcohol, acetone, or aniline; its *platinichloride* forms short, thick prisms.



crystallises in colourless needles, decomposes when slowly heated, but melts at 298—300° (corr.) if rapidly heated, is easily soluble in hot acetone or hot aniline, and moderately so in hot alcohol; its hydrochloride is instantly dissociated by water.

6-Bromo-4-keto-2-ethyldihydroquinazoline forms slender, prismatic needles, softens at 263°, melts at 267—268.5° (corr.), and behaves towards solvents like the methyl homologue.

6-Bromo-4-keto-2-isopropyldihydroquinazoline crystallises in colourless, prismatic needles, and, when rapidly heated, melts at 259—260.5° (corr.).

6-Bromo-4-keto-2-isobutyldihydroquinazoline forms small, prismatic needles, softens at 250°, and melts and decomposes slightly at 253—254° (corr.).

6-Bromo-4-keto-2-isoamyldihydroquinazoline crystallises in prismatic

needles, melts at 235—236° (corr.), is easily soluble in hot aniline, and moderately so in hot alcohol.

6-Bromo-4-keto-3-phenyl-2-methyldihydroquinazoline crystallises from alcohol in colourless, six-sided prisms and melts at 185—186° (corr.).

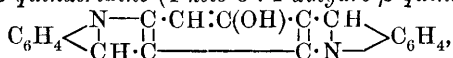
6-Bromo-4-keto-3-o-tolyl-2-methyldihydroquinazoline forms colourless crystals and melts at 137—138° (corr.).

Attention is drawn to the fact that with the exception of the methyl derivative, the melting points of these quinazolines fall regularly as the molecular weight increases, and that those of the *iso*-compounds are higher than those of the corresponding *n*-compounds. E. G.

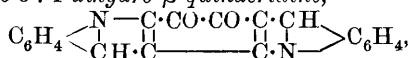
Quinazoline Alkyl Haloids. SIEGMUND GABRIEL and JAMES COLMAN (D.R.-P. 161401).—Quinazoline-3-methylum hydroxide (Abstr., 1904, i, 1060) dissolves in concentrated hydrochloric acid to form the *chloride* melting at 171—172°. The *bromide* dissolves in water and melts at 150—152°. The *hydroxide* prepared from quinazoline ethiodide is insoluble in cold water, but dissolves in hot water and melts at 145—146°; the *chloride* melts at 150—151°. The salts find therapeutic application. C. H. D.

Hydroxyquinacridine and Phloroquinyl. STEFAN VON NIEMENTOWSKI (*Ber.*, 1906, 39, 385—392. Compare Abstr., 1896, i, 261; Eliasberg and Friedländer, Abstr., 1892, 1106).—When heated to 115—120°, a mixture of 2 mols. of *o*-aminobenzaldehyde and 1 mol. of phloroglucinol develops heat and forms hydroxy- β -quinacridine together with small amounts of dihydroxyacridine and of phloroquinyl, which is formed as the chief product of the interaction of 3 mols. of *o*-aminobenzaldehyde with 1 mol. of phloroglucinol.

4-Hydroxy- β -quinacridine (4-keto-3 : 4-dihydro- β -quinacridine),



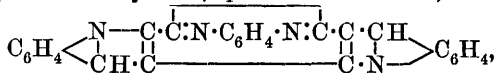
crystallises from glacial acetic acid in glistening, black needles containing $3\text{C}_2\text{H}_4\text{O}_2$, which is lost at 125°; it melts at 360°, is readily soluble in boiling glacial acetic acid, but only sparingly so in water, chloroform, carbon tetrachloride, or benzene, forming brownish-yellow, or in alcohol, ether, or acetone, emerald-green, solutions; the solution in nitrobenzene is brownish-yellow, and becomes emerald-green when heated. It is only very sparingly soluble in aqueous ammonia, alkali hydroxides, or dilute acids, but dissolves in concentrated sulphuric acid to form a green solution having a slight fluorescence. 4-Acetoxy- β -quinacridine, $\text{C}_{20}\text{H}_{11}\text{ON}_2\text{Ac}$, crystallises from nitrobenzene in slender, glistening, almost black needles with steel-blue lustre and melts at 300°. When oxidised with sodium dichromate in boiling glacial acetic acid solution, 4-hydroxy- β -quinacridine yields 3 : 4-diketo-3 : 4-dihydro- β -quinacridine,



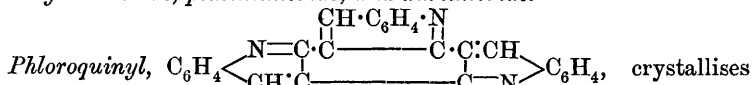
which crystallises in long, golden-yellow leaflets, becomes black and melts about 410°, and dissolves in concentrated sulphuric acid to form a golden-yellow solution, or in boiling methyl alcohol containing

a drop of concentrated aqueous potassium hydroxide solution, forming a dark-coloured solution; this does not change in colour when shaken with air (compare Bamberger, Abstr., 1885, 807).

When heated with *o*-phenylenediamine in glacial acetic acid solution, diketoquinacridine yields β -quinacrid-3:4-azine,



which crystallises from nitrobenzene in yellow needles, melts, becomes black, and forms a crystalline sublimate at 420°, and is only sparingly soluble in the ordinary solvents, but dissolves in concentrated sulphuric or hydrochloric acid to form a yellow solution; it forms a crystalline *hydrochloride*, *platinichloride*, and *aurichloride*.



from nitrobenzene in yellow or light brown needles, melts at 403°, is moderately soluble in boiling nitrobenzene, but is only sparingly so or is insoluble in other organic solvents, and is insoluble in dilute alkali hydroxides or acids, but dissolves in concentrated sulphuric acid, forming a yellow solution. It remains unchanged when heated with concentrated hydrochloric acid in a sealed tube at 200°, or when distilled over zinc dust, or when treated with sodium amalgam. It forms a red *nitro-derivative* when boiled with concentrated nitric acid, *additive* and *substitution* products when acted on by bromine with, or in the absence of, a solvent, and an unstable *additive* compound with methyl sulphate, which yields the phloroquinyl when boiled with aqueous potassium hydroxide.

G. Y.

Oxidation Products of *o*-Aminophenols. FRIEDRICH KEHRMANN (*Ber.*, 1906, 39, 134—138).—[With M. MATTISSON].—Air is passed through a hot aqueous solution of *o*-aminophenol until the amount of precipitate no longer increases, and the product removed, dried, and extracted with boiling benzene in the presence of animal charcoal. The benzene solution yields a mixture of two azine derivatives, which may be separated by acetylation and crystallisation of the acetyl derivatives from glacial acetic acid. The acetylaminophenoxazone, which is present in larger quantity, forms large, brownish-red plates and melts at 275°; the isomeric compound is less soluble, forms brick-red needles, and melts at 285°. Both acetyl derivatives are decomposed by 50 per cent. sulphuric acid, yielding, on the addition of water, brownish-blood-red solutions.

The solution from the compound melting at 285° reacts with nitrous acid with a brisk evolution of gas, but no indication of a precipitate. The isomeric compound under similar treatment yields no gas, but forms an orange-red *precipitate*, $\text{C}_{12}\text{H}_7\text{O}_3\text{N}_3$, which crystallises from a mixture of alcohol and benzene in yellowish-red needles decomposing at 175°.

[With W. URECH].—When *o*-amino-*o*-cresol is oxidised in a similar manner, it yields orange-red, glistening crystals, $\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2$, which

separate from a mixture of alcohol and benzene as red prisms with a violet, metallic lustre. The *hydrochloride* forms brownish-black needles. With nitrous acid, an orange-coloured precipitate is obtained.

[With E. BÜHLER.]—*o*-Amino-*m*-cresol yields orange-red crystals, C_7H_7ON , with a blue fluorescence; they melt at 176° and dissolve sparingly in water, but readily in organic solvents. The compound is decidedly basic; the *hydrochloride*, $(C_7H_7ON)_2 \cdot HCl$, forms brown crystals; the *platinichloride* is insoluble in water and forms brownish-red crystals; the *dichromate*, $C_{28}H_{30}O_4N_4Cr_2O_7$, forms red crystals; the *nitrate*, $C_{14}H_{15}O_2N_2NO_3$, forms red needles which dissolve readily in water. The base cannot be reduced readily. J. J. S.

Chemical and Thermochemical Researches on the Constitution of the Rosanilines. JULES SCHMIDLIN (*Ann. Chim. Phys.*, 1906, [viii], 7, 195–279).—A *résumé* of work already published in Abstr., 1903, i, 687; ii, 530, 633; 1904, i, 698, 785, 943, 944, 945, 1061; 1905, i, 75, and ii, 11 and 12. T. A. H.

Indamines and Thiazines. ROBERT GNEHM and W. SCHRÖTER (*J. pr. Chem.*, 1906, [ii], 73, 1–20. Compare Gnehm, Bot, and Weber, Abstr., 1902, i, 831; Gnehm and Bot, Abstr., 1904, i, 451; Gnehm and Weber, *ibid.*, 532; Gnehm and Kaufler, *ibid.*, 687, 935).—*p*-Amino-derivatives of methyl- and ethyl-anilines and of methyl- and ethyl-*o*-toluidines are prepared by formation of the nitrosoamines, conversion of these into the *p*-nitroso-derivatives by means of alcoholic hydrochloric acid and ether in the case of the aniline derivatives, or of concentrated aqueous hydrochloric acid with the derivatives of *o*-toluidine, and reduction of the nitroso-compounds with zinc and hydrochloric acid.

p-Aminomethyl-*o*-toluidine, $NH_2 \cdot C_6H_3Me \cdot NHMe$, is obtained as a colourless, viscid oil which does not solidify at -20° , boils at $276-276.5^\circ$ (corr.), and becomes brown owing to oxidation when exposed to the air. The *sulphate*, $(C_8H_{12}N_2)_2 \cdot H_2SO_4$, crystallises from dilute alcohol in slender, white needles.

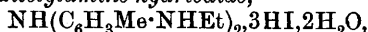
s-Di-*p*-methylaminodiphenylamine, $NH(C_6H_4 \cdot NHMe)_2$, is formed by oxidation with aqueous sodium hypochlorite of a mixture of methyl-aniline and *p*-phenylenemethyldiamine, and reduction of the resulting solution with zinc dust. It crystallises in glistening, colourless leaflets or needles, melts at 115° (corr.), is easily soluble in chloroform or acetone, but less so in ether, alcohol, benzene, toluene, or hot light petroleum, and when moist is oxidised rapidly by the air, becoming yellow to brownish-blue. The *hydrochloride*, $C_{14}H_{17}N_3 \cdot 2HCl$, forms brown leaflets, froths at 220° , and melts at $225-227^\circ$ (corr.). The *triacetyl* derivative, $C_{14}H_{14}N_3Ac_3$, melts at 245° (corr.).

Di-*p*-ethylaminodiphenylamine, $NH(C_6H_4 \cdot NHEt)_2$, formed from ethylaniline and *p*-phenylene-ethyldiamine, melts at 95° (corr.) and is more readily soluble than the *s*-dimethyl compound. The *hydrochloride*, $C_{16}H_{21}N_3 \cdot 2HCl$, melts at $217-218^\circ$ (corr.). The *triacetyl* derivative, $C_{16}H_{13}N_3Ac_3$, melts at 207° (corr.).

As they undergo oxidation with great ease, the *s*-dialkyl-leucindamines, formed from ethyl-*o*-toluidine and ethyl-*p*-tolylenediamine and

from methyl-*o*-toluidine and methyl-*p*-tolylenediamine, cannot be isolated except in the form of salts or derivatives.

Di-p-ethylaminoditolylamine hydriodide,



crystallises in glistening, orange leaflets and melts at 120—122° (corr.). The *tribenzoyl* derivative, $\text{C}_{18}\text{H}_{22}\text{N}_3\text{Bz}_3$, formed by the action of benzoyl chloride and sodium hydroxide on the hydriodide, is obtained as a white, glutinous powder, which becomes soft at 60° and melts above 90°.

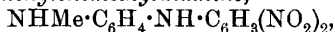
Di-p-methylaminoditolylamine hydriodide, $\text{NH}(\text{C}_6\text{H}_3\text{Me}\cdot\text{NHMe})_2, 2\text{HI}$, crystallises in sheaves of slender, white needles and melts at 242°. The *tribenzoyl* derivative, $\text{C}_{16}\text{H}_{16}\text{N}_3\text{Bz}_3$, resembles that of the *s*-diethyl compound.

Trinitrophenyl-p-phenylenemethyldiamine,



is formed by boiling *p*-phenylenemethyldiamine with picryl chloride and potassium acetate in alcoholic solution in a reflux apparatus; it crystallises in dark brownish-red, glistening leaflets, melts at 188° (corr.), and when condensed with sulphur chloride in presence of potassium acetate yields a mixture of *products* from which no one could be isolated.

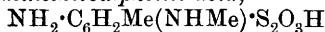
Dinitrophenyl-p-phenylenemethyldiamine,



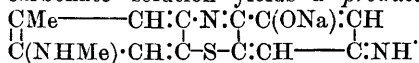
formed from *p*-phenylenemethyldiamine and 1-chloro-2:4-dinitrobenzene, melts at 153°.

The action of sulphur chloride on di-*p*-ethyldiaminodiphenylamine in benzene solution leads to the formation of a labile additive compound, which is obtained as a green precipitate, becoming greyish-green on drying.

Tolylene-methyldiaminethiosulphonic acid,



[Me:NHMe:S₂O₃H:NH₂=1:2:4:5], is formed by adding acetic acid and potassium dichromate to a mixture of *p*-methylamino-*o*-toluidine sulphate, aluminium sulphate, and sodium thiosulphate in aqueous solution. It forms green crystals, melts at 212—213°, and when oxidised with sodium hypochlorite in dilute aqueous sodium carbonate solution yields a *product* which may be the thiazine,



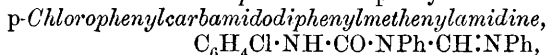
Aminoleucomethylene-blue, $\text{C}_{16}\text{H}_{20}\text{N}_4\text{S}$, is formed by reduction of methylene-green (nitromethylene-blue) with zinc dust and acetic acid. It crystallises in sheaves of slightly green needles, melts at 143—145°, and is very easily oxidised, so that it can be obtained only with complete exclusion of air.

G. Y.

Phenylcarbamidodiphenylmethenylamidine and its easy Decomposition with Formation of Phenylcarbimide. REINHOLD VON WALTHER (*J. pr. Chem.*, 1906, [ii], 73, 108—112).—*Phenylcarbamidodiphenylmethenylamidine*, $\text{NHPh}\cdot\text{CO}\cdot\text{NPh}\cdot\text{CH}\text{:}\text{NPh}$, is formed when diphenylmethenylamidine is heated with phenylcarbimide on the water-bath. It crystallises from light petroleum in small, stout, transparent prisms, melts at 104°, and is readily soluble in the

ordinary solvents when warm. *s*-Diphenylcarbamide melts at 235°, and diphenylmethylcarbamide at 104°. A table is given to show that the introduction of aliphatic groups into phenyl- or *s*-diphenylcarbamide depresses the melting point, the ethyl group effecting the fusibility to a greater extent than the methyl group, and that the melting point rises again slowly as successive methyl groups are introduced.

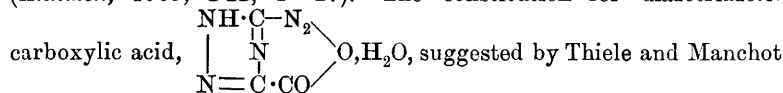
Phenylcarbamidodiphenylmethenylamidine decomposes slowly at the laboratory temperature with formation of *s*-diphenylcarbamide, or quickly when boiled with alcohol, with formation of diphenylmethenylamidine and ethyl phenylcarbamate; it interacts with aniline with development of heat and formation of *s*-diphenylcarbamide, or with *p*-chloroaniline to form *p*-chloro-*s*-diphenylcarbamide.



formed from diphenylmethenylamidine and *p*-chlorophenylcarbamide, crystallises from light petroleum in white, prismatic needles, melts at 97—103°, and interacts with aniline to form *p*-chloro-*s*-diphenylcarbamide, or with *p*-chloroaniline to form *s*-di-*p*-chlorophenylcarbamide.

Diphenylmethylcarbamide and complex carbamides, such as 1-phenylcarbamido-2-methylindole, do not interact with aniline at the laboratory temperature. G. Y.

Derivatives of Triazole. WILHELM MANCHOT and R. NOLL (*Annalen*, 1905, 343, 1—27).—The constitution for diazotriazole-



(*Abstr.*, 1899, i, 167), represents the compound as an internal anhydride. Since, however, the ester of aminotriazolecarboxylic acid yields an analogous diazo-compound, which is obviously unable to form such an anhydride, it is more probable that the acid above mentioned is represented by the formula $\text{NH}\begin{array}{c} \text{N} \\ \diagup \\ \text{C}(\text{NH}\cdot\text{NO})\cdot\text{N} \\ \diagdown \\ \text{C}=\text{N} \end{array} \text{CO}_2\text{H}$.

Diazotriazolecarboxylic acid is best prepared by adding to sodium aminotriazolecarboxylate, first, concentrated hydrochloric acid, and then at -4° a solution of sodium nitrite. The *ethyl* ester is prepared in a similar manner by diazotising ethyl aminotriazolecarboxylate; it is very explosive.

It is to be noted that chlorotriazole (*loc. cit.*) does not lose chlorine when treated either with nascent hydrogen or nitric acid. *Bromotriazole*, $\text{NH}\begin{array}{c} \text{N}=\text{CH} \\ \diagup \\ \text{CBr}\cdot\text{N} \end{array}$, is prepared by pouring fuming hydrobromic acid over the diazo-acid rubbed up with a little water; it crystallises in prisms melting at 188—189°, and by sodium amalgam is converted into triazole. With silver nitrate it gives a white, and with copper acetate a pale blue, precipitate. Diazotriazolecarboxylic acid reacts with aqueous potassium iodide, iodine being set free and triazole and *iodotriazole* formed. The latter crystallises in needles melting and

decomposing at 208° , iodine being liberated; with silver nitrate and copper acetate, it gives precipitates similar to those formed from the bromotriazole, and by sodium amalgam it is reduced to triazole.

Hydroxytriazolecarboxylic acid (Abstr., 1899, i, 84) can be obtained from the diazo-acid and acetic acid; at first orange-red needles of the anhydrous acid are formed, which gradually pass into the crystals of the hydrated acid. When reduced at a low temperature with stannous chloride and hydrochloric acid, diazotriazolecarboxylic acid is converted into *triazylhydrazine*, $\text{NH} \begin{array}{c} \text{N}=\text{CH} \\ \diagup \quad \diagdown \\ \text{C}(\text{N}_2\text{H}_3):\text{N} \end{array}$, the *hydrochloride* of

which crystallises in needles melting and decomposing at 224° . The *picrate* crystallises in pale yellow needles melting at 165° . *Benzylidene-triazylhydrazone* crystallises in needles melting at $225.5\text{--}226^{\circ}$; the corresponding *salicyl* derivative melts and decomposes at 259° ; the *acetophenone* derivative forms small plates, melting at 276° , and the *acetone* derivative melts at 216° .

Triazylazoimide, $\text{NH} \begin{array}{c} \text{N}=\text{CH} \\ \diagup \quad \diagdown \\ \text{C}(\text{N}_3):\text{N} \end{array}$, prepared from the hydrazine hydrochloride and sodium nitrite, forms crystals melting at $121\text{--}122^{\circ}$ and yields an explosive *silver* salt.

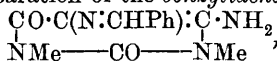
Nitrohydroxytriazole, $\text{NH} \begin{array}{c} \text{N}=\text{C}\cdot\text{OH} \\ \diagup \quad \diagdown \\ \text{C}(\text{NO}_2):\text{N} \end{array}$, prepared when hydroxy-triazole is treated with fuming nitric acid, forms crystals decomposing at 254° ; its *silver* salt is a pale yellow, crystalline precipitate exploding when heated. When nitrohydroxytriazole is reduced with tin and hydrochloric acid, the corresponding *aminohydroxytriazole* is produced. Its *hydrochloride* is crystalline and melts at 196° , and the *picrate* crystallises in pale yellow needles melting at 204° ; the *silver* salt is red, and gives a silver mirror when heated.

K. J. P. O.

Preparation of 4:5-Diamino-2:6-dihydroxypyrimidine and its Derivatives. EMANUEL MERCK (D.R.-P. 161493).—5-isoNitroso-4-amino-2:6-dihydroxy-3-methylpyrimidine (Traube, Abstr., 1900, i, 416; 1901, i, 54) may be reduced to 4:5-diamino-2:6-dihydroxy-3-methylpyrimidine in sulphuric acid solution by means of iron or zinc dust. Ammonia precipitates the base in bright yellow needles from a hot solution of the sulphate. 4:5-Diamino-2:6-dihydroxypyrimidine and its 1:3-dimethyl derivative may be prepared in similar manner.

C. H. D.

Action of Aldehydes on o-Diamines of the Pyrimidine Series. WILHELM TRAUBE and WALTHER NITHACK (*Ber.*, 1906, 39, 227—235. Compare Abstr., 1900, i, 416; 1901, i, 54; 1904, i, 632; Gabriel and Cplman, Abstr., 1901, i, 427).—Benzaldehyde (1 mol.) when added to an aqueous solution of 4:5-diamino-2:6-dioxy-1:3-dimethylpyrimidine (1 mol.) causes the separation of the *benzylidene* compound,



which is easily hydrolysed by acids into its constituents. On heating this compound with a second molecular proportion of benzaldehyde, 8-phenyl-7-benzyl-1:3-dimethylxanthine is obtained. Oxidation of

the benzylidene compound with ferric chloride produces 8-phenyl-theophylline.

4-Amino-5-benzylideneamino-2:6-dioxy-3-methylpyrimidine,
 $C_{12}H_{12}O_2N_4$,

crystallises from hot alcohol in delicate needles which melt and decompose at 274° . It is insoluble in water or cold alcohol and is hydrolysed into its constituents by mineral acids. Ammoniacal solutions of silver salts are vigorously reduced by it, and on evaporation with nitric acid a reddish-purple residue is obtained. The corresponding *hydroxy-benzylidene* compound, obtained from salicylaldehyde, forms long, yellow needles.

8-Phenyl-7-benzyl-3-methylxanthine, $C_{19}H_{16}O_2N_4$, obtained by heating the benzylidene compound (1 mol.) described previously and benzaldehyde (1 mol.) at 180° , separates from alcohol in yellow crystals which are unaffected by boiling acids and dissolve in alkalis to a yellow solution from which acids reprecipitate the substance unchanged.

3-Methylxanthine is prepared by warming a solution of 4:5-diamino-2:6-dioxy-3-methylpyrimidine in acetic acid, adding a solution of formaldehyde, and subsequently oxidising the condensation product formed by means of ferric chloride. In all its properties and colour reactions, the substance is identical with the 3-methylxanthine obtained by E. Fischer (Abstr., 1898, i, 700) and by Traube (*loc. cit.*).

8-Hydroxyphenyl-3-methylxanthine, $C_{12}H_{10}O_3N_4$, is obtained like the preceding compound, employing salicylaldehyde in the place of formaldehyde. It separates from alcohol in colourless needles which do not possess reducing properties and are not acted on by acids. By evaporation with nitric acid, a yellow-coloured residue is formed.

3-Methyl-8-isobutylxanthine, $C_{10}H_{14}O_2N_4$, obtained in similar manner from valeraldehyde, separates from hot water in minute, colourless needles.

4-Amino-5-benzylideneamino-2:6-dioxy-1:3-dimethylpyrimidine,
 $C_{13}H_{14}O_2N_4$,

separates from alcohol in orange-yellow needles which melt and decompose at 220° . It is hydrolysed by mineral acids and reduces ammoniacal solutions of silver salts.

8-Phenyl-7-benzyl-1:3-dimethylxanthine, $C_{20}H_{18}O_2N_4$, obtained by fusing the preceding compound with an equivalent quantity of benzaldehyde, has a bright yellow colour, melts and decomposes at 221° , and is unaffected by mineral acids.

8-Phenyl-1:3-dimethylxanthine, $C_{13}H_{12}O_2N_4$, obtained from the benzylidene compound by oxidation with ferric chloride, crystallises from acetic acid in colourless, rhombic plates, insoluble in water or alcohol, and remains unchanged at 300° . It does not possess reducing properties and is practically unaffected by acids.

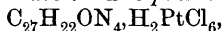
8-Hydroxyphenyl-7-hydroxybenzyl-1:3-dimethylxanthine, $C_{20}H_{18}O_4N_4$, obtained from the pyrimidine base and 2 mols. of salicylaldehyde at 180° , forms a yellow, crystalline powder. The intermediate *hydroxy-benzylidene* compound (from 1 mol. of salicylaldehyde) crystallises in yellow needles which decompose at 242° .

1:3-Dimethyl-8-isobutylxanthine, $C_{11}H_{16}O_2N_4$, separates from hot aqueous solution in colourless needles melting at 227° . It is stable towards acids and does not possess reducing properties.

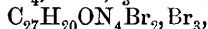
8-Phenyl-7-benzylguanine, $C_{18}H_{15}ON_5$, is obtained by heating at 180° 2:4:5-triamino-6-oxypyrimidine and benzaldehyde (2 mols.). It separates from hot alcohol in light yellow needles. The intermediate *benzylidene* compound (from 1 mol. of benzaldehyde) crystallises in yellow needles which melt and decompose at 276° and is easily hydrolysed by mineral acids. C. S.

Action of Phosphorus Oxychloride on Bispyrazolone Derivatives of Aldehydes and Ketones. AUGUST MICHAELIS and ADALBERT ZILG (*Ber.*, 1906, 39, 370—381. Compare Abstr., 1905, i, 377, 392). — 4:4'-Benzenyl-1:3:5-phenylmethylpyrazolone-1':3'-phenylmethylpyrazole,
$$\begin{array}{c} \text{NPh} \cdot \text{CO} \\ | \\ \text{N} - \text{CMe} \end{array} > \text{C} : \text{CPh} \cdot \text{CH} < \begin{array}{c} \text{CH} - \text{NPh} \\ | \\ \text{CMe} : \text{N} \end{array}$$
, is formed when

benzylidenebis-1:3:5-phenylmethylpyrazolone (Lachowicz, Abstr., 1897, i, 119) is heated with phosphorus oxychloride at 135 — 140° and the product poured into water and treated with dilute sodium hydroxide. It crystallises from alcohol or ethyl acetate in slender, white needles, melts at 196° , has feeble basic properties, is readily soluble in hot alcohol, ethyl acetate, chloroform, ether, or benzene, and dissolves in concentrated hydrochloric acid, from which it separates unchanged on addition of water. The *platinichloride*,

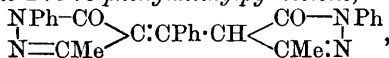


forms slender, yellow needles and melts above 260° ; the *aurichloride*, $C_{27}H_{22}ON_4 \cdot HAuCl_4$, crystallises in yellow needles and melts at 218° ; the *methiodide*, $C_{27}H_{22}ON_4 \cdot 2MeI \cdot 3H_2O$, crystallises from alcohol and forms a *periodide*, $C_{27}H_{22}ON_4 \cdot 2MeI \cdot I_8$. The *perbromide*,



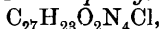
formed by the action of an excess of bromine on the base in glacial acetic acid solution, crystallises in yellow needles and when treated with hot dilute sodium hydroxide loses bromine and yields the *dibromide*, $C_{27}H_{20}ON_4Br_2$, which crystallises in slender needles and melts at 219° . The *nitro-derivative*, $C_{27}H_{21}ON_4 \cdot NO_2$, formed by the action of fuming nitric acid on the base, crystallises from glacial acetic acid and melts at 235 — 243° .

4:4'-Benzenylbis-1:3:5-phenylmethylpyrazolone,



is formed by the action of phosphorus pentachloride on benzenyl-phenylmethylpyrazolonephenylmethylpyrazole at 140° or by oxidation of this with potassium permanganate and sulphuric acid below 30° . It crystallises in yellow needles, melts at 242° , and dissolves in aqueous alkali hydroxides to form a dark red solution, or in concentrated hydrochloric acid, from its solution in which it is precipitated on dilution with water. The ammonium and barium derivatives are red; the *silver* derivative, $C_{27}H_{21}O_2N_4Ag$, forms dark red, nodular crystals.

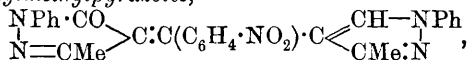
4:4'-p-Chlorobenzenylbis-1:3:5-phenylmethylpyrazolone,



is formed by heating phenylmethylpyrazolone with *p*-chlorobenzaldehyde; it crystallises from alcohol in slender, white needles, melts and becomes red at 213° , and is readily soluble in alcohol, chloroform,

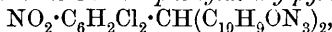
dilute acids, or aqueous alkali hydroxides. When heated with phosphorus oxychloride in a sealed tube at 145° for ten hours, it yields 4 : 4'-p-chlorobenzoyl-1 : 3 : 5-phenylmethylpyrazolone-1 : 3-phenylmethylpyrazole, $\begin{array}{c} \text{NPh} \cdot \text{CO} \\ | \\ \text{N} = \text{CMe} \end{array} > \text{C} : \text{C}(\text{C}_6\text{H}_4\text{Cl}) \cdot \text{CH} < \begin{array}{c} \text{CH} - \text{NPh} \\ | \\ \text{CMe} : \text{N} \end{array}$, which crystallises in needles, melts at 213° , is insoluble in dilute aqueous alkali hydroxides, and when treated with phosphorus pentachloride yields a product, $\text{C}_{27}\text{H}_{21}\text{O}_2\text{N}_4\text{Cl}$. This crystallises in yellowish-red needles, sinters at 185° , and melts at 211° .

Phenylmethylpyrazolone condenses with *o*- and with *m*-nitrobenzaldehyde to form the corresponding nitrobenzoylbisphenylmethylpyrazolones, $\text{C}_{27}\text{H}_{23}\text{O}_4\text{N}_5$; these form yellowish-green crystals; the *m*-compound melts at 230° ; the *o*-compound, which is readily soluble in benzene, melts at 226° . When heated with phosphorus oxychloride, the bispyrazolones form the corresponding nitrobenzoylphenylmethylpyrazolonephenylmethylpyrazoles,



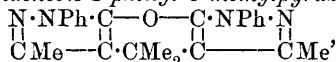
which are insoluble in aqueous alkali hydroxides. The *m*-compound forms colourless crystals and melts at 240° ; the *o* compound forms green crystals and melts at 237° . When treated with phosphorus pentachloride, these substances yield oxidation products, $\text{C}_{27}\text{H}_{21}\text{O}_4\text{N}_5$, of which the *m*-derivative melts at 183° and the *o*-compound at 207° .

2 : 4 : 6-Trinitrobenzaldehyde does not condense with phenylmethylpyrazolone, but 2 : 5-dichloro-6-nitrobenzaldehyde interacts with the pyrazolone to form a mixture of 2 : 5-dichloro-6-nitrobenzylidene-1 : 3' : 5-phenylmethylpyrazolone, $\text{C}_{10}\text{H}_8\text{ON}_2 \cdot \text{CH} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{NO}_2$, which crystallises in yellowish-red needles and melts at 139° , and 2 : 5-dichloro-6-nitrobenzylidenebis-1 : 3 : 5-phenylmethylpyrazolone,



which forms dark yellow crystals, melts at 250° , and when treated with phosphorus oxychloride yields a product insoluble in aqueous alkali hydroxides.

Anhydroisopropylidenebis-1-phenyl-3-methylpyrazolone,



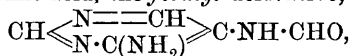
is formed by heating 4-isopropylenebis-1-phenylmethylpyrazolone (Knorr, Abstr., 1887, 602) with phosphorus oxychloride in a sealed tube at 125 — 130° ; it forms colourless crystals, melts at 163° , boils with only slight decomposition at 400 — 405° , and is insoluble in aqueous alkali hydroxides, but dissolves in concentrated sulphuric acid. The platinumchloride, $\text{C}_{23}\text{H}_{22}\text{ON}_4 \cdot \text{H}_2\text{PtCl}_6$, melts above 300° ; the yellow, crystalline aurichloride, $\text{C}_{23}\text{H}_{22}\text{ON}_4 \cdot \text{HAuCl}_4$, melts at 256° ; the methiodide, $\text{C}_{23}\text{H}_{22}\text{ON}_4 \cdot \text{MeI}$, crystallises in slender needles and melts at 213° ; the dimethiodide, $\text{C}_{23}\text{H}_{22}\text{ON}_4 \cdot 2\text{MeI} \cdot 2\text{H}_2\text{O}$, crystallises from hot water in needles and decomposes with formation of the monomethiodide at 150 — 160° . With bromine in glacial acetic acid solution, the anhydro-base forms a perbromide, which crystallises in slender, yellow needles, and when treated with aqueous alkali hydroxides forms the dibromo-derivative, $\text{C}_{23}\text{H}_{20}\text{ON}_4\text{Br}_2$, crystallising

in slender, glistening, colourless needles and melting at 239° . The dinitro-derivative, $C_{23}H_{20}ON_4(NO_2)_2$, crystallises in yellow needles and melts at 290° . When heated on the water-bath with phosphorus pentachloride, the anhydro-base yields 4:5-dichloro-1-phenyl-3-methylpyrazole (Michaelis and Pasternack, Abstr., 1899, i, 941).

Butyridenebis-1-phenyl-3-methyl-5-pyrazolone, $C_{24}H_{26}O_2N_4$, is formed by heating phenylmethylpyrazolone with methyl ethyl ketone; it separates from alcohol in colourless crystals, melts at 248° , is readily soluble in alcohol, aqueous alkali hydroxides, or acids, and when heated with phosphorus oxychloride at $125-130^{\circ}$ yields the *anhydro-base*, $\begin{array}{c} N \cdot NPh \cdot C - O - C \cdot NPh \cdot N \\ | \quad \quad | \quad \quad | \\ CMe - C \cdot CMeEt - C - CMe \end{array}$, which separates from alcohol in colourless crystals, melts at 182° , and is insoluble in aqueous alkali hydroxides. G. Y.

Synthesis of Purine. OSKAR ISAY (*Ber.*, 1906, 39, 250—265).—

2:4-Dichloro-5-nitropyrimidine, $CCl \begin{array}{c} N:CH \\ \diagdown \quad \diagup \\ N \cdot CCl \end{array} > C \cdot NO_2$, prepared by heating 5-nitrouracil with phosphorus oxychloride containing a little hydrochloric acid for about twenty minutes at 185° , crystallises from alcohol, ether, or light petroleum in lustrous leaflets, melts at 29.3° , and boils at $153-155^{\circ}$ under 58 mm. pressure. By cold alcoholic ammonia, it is converted into 2-chloro-5-nitro-4-aminopyrimidine, $CCl \begin{array}{c} N=CH \\ \diagdown \quad \diagup \\ N \cdot C(NH_2) \end{array} > C \cdot NO_2$, which crystallises from water in white, silky, four-sided prisms, darkens at 205° , decomposes at 217° , and is reduced by hydriodic acid and phosphonium iodide to 4:5-diaminopyrimidine, $CH \begin{array}{c} N=CH \\ \diagdown \quad \diagup \\ N \cdot C(NH_2) \end{array} > C \cdot NH_2$; this crystallises from water in aggregates of slender needles, melts at 202.5° , boils at 229° under 32 mm. pressure, and gives the following crystalline salts: the *hydrochloride*, *hydrobromide*, *aurichloride*, *platinichloride*, $2C_4H_6N_4, H_2PtCl_6$; the *picrate* decomposes at 264° . On heating 4:5-diaminopyrimidine with anhydrous formic acid, the *formyl* derivative,



is obtained; it crystallises from alcohol in white leaflets, melts at 198° , and at a higher temperature loses water, giving purine. The latter substance can be prepared directly from 4:5-diaminopyrimidine by heating it with anhydrous formic acid, evaporating the excess of the latter, and subliming the product under reduced pressure.

8-Methylpurine, $\begin{array}{c} N:CH \cdot C \cdot NH \\ | \quad \quad | \\ CH:N \cdot C - N \end{array} > CMe$, prepared by heating 4:5-diaminopyrimidine with acetic anhydride at 210° and distilling the product, solidifies in stellar aggregates of needles and melts at $265-266^{\circ}$; the *hydrochloride*, *hydriodide*, and *platinichloride*, $C_6H_6N_4, H_2PtCl_6$, are crystalline.

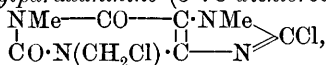
On heating 4:5-diaminopyrimidine with carbamide at 165° , it is converted into 8-oxypurine (Fischer and Ach, Abstr., 1898, i, 47). Substituting thiocarbamide for carbamide, 8-thiopurine, $C_5H_4N_4S$, is

obtained; this crystallises from alcohol in lanceolate needles and begins to decompose at 268° . On melting 4:5-diaminopyrimidine with benzil at 175° , the *azine*, $\begin{array}{c} \text{N} \cdot \text{CH} \cdot \text{C} \cdot \text{N} \cdot \text{CPh} \\ | \quad | \quad | \\ \text{CH} \cdot \text{N} \cdot \text{C} \cdot \text{N} \cdot \text{CPh} \end{array}$, is formed; it crystallises from alcohol in small, yellow plates and melts at 170.5° .

5-Nitro-2:4-diaminopyrimidine, $\text{NH}_2 \cdot \text{C} \begin{array}{c} \text{N} = \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{C}(\text{NH}_2) \end{array} \text{C} \cdot \text{NO}_2$, prepared by heating 2:4-dichloro-5-nitropyrimidine with alcoholic ammonia for two hours at 100° , crystallises from water, in which it is very slightly soluble, in white, rhombic prisms and does not melt at 260° ; the *hydrochloride*, *platinichloride*, *aurichloride*, and *picrate* are crystalline; the *sulphate* melts at 201° and the *nitrate* at 213° . On reducing the base with stannous chloride and hydrochloric acid, 2:4:5-triaminopyrimidine is obtained; it forms slender needles, may be distilled under reduced pressure, sinters at 176° , and melts at 179° ; the *hydrochloride*, *platinichloride*, *sulphate*, and *nitrate* are crystalline, and the *picrate*, $\text{C}_4\text{H}_7\text{N}_5 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, decomposes at 264° . On heating 2:4:5-triaminopyrimidine with formic acid, the *formyl* derivative, $\text{NH}_2 \cdot \text{C} \begin{array}{c} \text{N} = \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{C}(\text{NH}_2) \end{array} \text{C} \cdot \text{NH} \cdot \text{CHO}$, is produced; it gives well-defined salts, melts at 224° , and at a higher temperature is converted by loss of water into 2-aminopurine or isoadenine, which appears to be identical with the substance described by Tafel and Ach (*Abstr.*, 1901, i, 426). 2-Aminopurine does not give the adenine reaction of Kossel and Fischer.

W. A. D.

Conversion of Caffeine into Paraxanthine, Theophylline, and Xanthine. EMIL FISCHER and FRIEDRICH ACH (*Ber.*, 1906, 39, 423—435. Compare *Abstr.*, 1896, i, 13).—A 30 per cent. yield of 8-chloro-3-chloromethylparaxanthine (3':8-dichlorocaffeine),



is formed when caffeine, or, better, 8-chlorocaffeine, is heated for eleven hours with a mixture of phosphorus oxychloride and pentachloride at 158 — 162° . A small amount of a trichlorocaffeine is formed at the same time. An 18 per cent. yield of the dichloro-compound is obtained when chlorine is led into the fused and well-stirred 8-chloro-derivative, first at 200° and then at 170° . It crystallises from a mixture of benzene and ether in nodular aggregates of needles melting at 145 — 146° (corr.), is readily soluble in cold chloroform, benzene, acetone, or ethyl acetate and in hot ether or alcohol, and gives the murexide reaction with chlorine water.

When boiled with water, the dichloro-derivative is decomposed, and formaldehyde, hydrogen chloride and chloroparaxanthine (*Abstr.*, 1899, i, 173) are formed.

8-Chloro-3'-methoxycaffeine, $\begin{array}{c} \text{NMe} - \text{CO} - \text{C} \cdot \text{NMe} \\ | \quad | \quad | \\ \text{CO} \cdot \text{N}(\text{CH}_2 \cdot \text{OMe}) \cdot \text{C} - \text{N} \end{array} \text{CCl}$, is

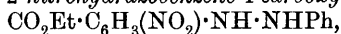
readily formed when the crude dichloro-compound is boiled with methyl alcohol. It crystallises in colourless, glistening needles, sinters at 126° , and melts at 130 — 131° (corr.), is very sparingly soluble in ether or

hot water, and when heated with fuming hydrochloric acid at 100° yields chloroparaxanthine.

7':8-Dichlorocaffeine, $\begin{array}{c} \text{NMe}-\text{CO}-\text{C} \cdot \text{N}(\text{CH}_2\text{Cl}) \\ \text{CO} \cdot \text{NMe} \cdot \text{C} \end{array} \xrightarrow{\text{N}} \text{CCl}$, is produced by the action of chlorine on a nitrobenzene or phosphorus oxychloride solution of chlorocaffeine at 90—100°. It crystallises from hot methyl alcohol in slender, colourless needles, melts at 150·5—152·5°, is readily soluble in glacial acetic acid or benzene, only sparingly so in hot alcohol, and dissolves in only 70 parts of boiling water. When boiled with ten times its weight of water, it yields 8-chlorotheophylline (Abstr., 1896, i, 263), and with an ethyl-alcoholic solution of sodium ethoxide, 7':8-diethoxycaffeine, $\text{C}_{12}\text{H}_{18}\text{O}_4\text{N}_4$. This crystallises in colourless, felted needles and melts at 125—126° (corr.). One gram dissolves in about 70 c.c. of warm ether, 10 c.c. of hot alcohol, 90 c.c. of boiling water, or 1250 c.c. of water at 23°.

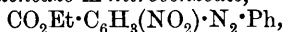
Tetrachlorocaffeine, $\begin{array}{c} \text{N}(\text{CH}_2\text{Cl})-\text{CO}-\text{C} \cdot \text{N}(\text{CH}_2\text{Cl}) \\ \text{CO} \cdot \text{N}(\text{CH}_2\text{Cl}) \cdot \text{C} \end{array} \xrightarrow{\text{N}} \text{CCl}$, is formed when 7':8-dichlorocaffeine is heated with a phosphorus oxychloride solution of chlorine at 160—162°. It crystallises from ether, melts at 129—130·5° (corr.), and dissolves readily in acetone, acetic acid, or benzene. When boiled with sodium methoxide in methyl-alcoholic solution, it yields tetramethoxycaffeine, $\text{C}_{12}\text{H}_{18}\text{O}_6\text{N}_4$, which melts at 119—121° (corr.) and dissolves only sparingly in cold ether or water. When boiled with dilute acetic acid, the methoxy-derivative yields chloroxanthine, and this, when reduced with hydriodic acid and phosphonium iodide, gives xanthine. J. J. S.

Condensation of Phenylhydrazine with Ethyl 4-Chloro-3-nitrobenzoate. ALFRED WERNER and W. PETERS (*Ber.*, 1906, 39, 185—192).—Ethyl 2-nitrohydrazobenzene-4-carboxylate,



is obtained together with phenylhydrazine hydrochloride when ethyl 4-chloro-3-nitrobenzoate is heated on the water-bath with pure colourless phenylhydrazine (2 mols.). It crystallises from alcohol, melts at 129°, and dissolves readily in alcohol, ether, or acetone.

When the alcoholic solution is oxidised with yellow mercuric oxide, it yields ethyl p-benzeneazo-m-nitrobenzoate,



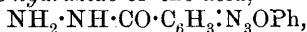
which crystallises in brilliant red needles melting at 139°. p-Benzene-azo-m-nitrobenzoic acid is obtained when the ester is hydrolysed with alcoholic potash. It crystallises from alcohol in red needles, melts at 215°, and dissolves in ether, alcohol, or benzene.

When ethyl 4-chloro-3-nitrobenzoate is heated at 90° with commercial phenylhydrazine, the product is ethyl phenylaznitrosobenzenecarboxylate,

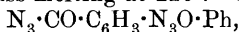
$\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \quad \text{O} \end{array} \text{NPh}$, which crystallises in long, colourless needles

melting at 105° and soluble in ether, alcohol, benzene, or acetic acid. The corresponding acid, $\text{C}_{13}\text{H}_9\text{O}_3\text{N}_3$, crystallises from dilute alcohol in colourless, glistening needles melting at 250° and is insoluble in

water. The *potassium* salt, $C_{13}H_8O_3N_3K$, crystallises from alcohol in slender needles. The *hydrazide* of the acid,

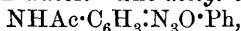


obtained by the action of hydrazine hydrate on the ester, forms a gelatinous, flocculent mass melting at 220° . The *azoimide*,



obtained by the action of nitrous acid on the hydrazide, crystallises from benzene in slender, yellow needles melting at 140° .

Phenylaznitrosobenzeneurethane, $CO_2Et \cdot NH \cdot C_6H_3 : N_3O \cdot Ph$, obtained by boiling the azoimide with absolute alcohol for five to six hours, crystallises in pale yellow needles and melts at 215° . When boiled with alcoholic sodium hydroxide, the urethane compound is hydrolysed to *aminophenylaznitrosobenzene*, $NH_2 \cdot C_6H_3 : N_3O \cdot Ph$, which crystallises from alcohol in greenish-yellow needles melting at 180° and readily soluble in organic solvents and also in hot water. The *hydrochloride* dissolves fairly readily in water. The *acetyl* derivative,

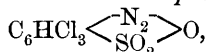


forms glistening needles and melts at 233° .

Ethyl phenylazimidobenzenecarboxylate, $CO_2Et \cdot C_6H_3 : N_3 \cdot Ph$, obtained by reducing ethyl phenylaznitrosobenzenecarboxylate with stannous chloride and hydrochloric acid, crystallises from alcohol in glistening needles melting at 84° and readily soluble in organic solvents. The corresponding *acid*, $C_{13}H_9O_2N_3$, sublimes in needles, melts at 232° , and dissolves readily in ether, alcohol, or acetic acid. J. J. S.

Substitution of Negative Groups by the Hydroxyl Group in Ortho-substituted Diazonium Salts. EMILIO NOELTING and MARTIN BATTEGAY (*Ber.*, 1906, 39, 79—86).—2 : 5 : 6-*Trichloroaniline-3-sulphonic acid*, formed by nitration and reduction of 2 : 4 : 5-trichlorobenzene-3-sulphonic acid, crystallises in white needles and is easily soluble in hot, but only sparingly so in cold, water. The *sodium*, $C_6H_3O_3NCl_3Na, H_2O$, and *barium* salts were analysed.

2 : 5 : 6-*Trichlorobenzenediazonium-3-sulphonic anhydride*,



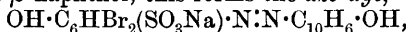
prepared by treating the sodium salt of the above acid with hydrochloric acid and sodium nitrite at $20-25^\circ$, is obtained as a brown, crystalline powder. It detonates when heated, does not give a precipitate with silver nitrate in aqueous solution, dissolves in concentrated sulphuric acid to form a red solution, and loses nitrogen when heated in aqueous or alcoholic solution. When "coupled" with β -naphthol, it forms the *sodium* salt, $SO_3Na \cdot C_6HCl_3 \cdot N : N \cdot C_{10}H_6 \cdot OH$, which crystallises from glacial acetic acid in glistening, orange needles, dissolves in concentrated sulphuric acid to form a carmine solution, and dyes wool orange. When treated with cuprous chloride in hydrochloric acid solution, the diazonium compound yields 2 : 3 : 4 : 5-*tetrachlorobenzenesulphonic acid*, which crystallises in white needles and is readily soluble in water. The *sodium* salt, $C_6HO_3Cl_4Na, H_2O$, crystallises in sheaves of white needles; the *barium* salt, $(\frac{1}{2}H_2O)$, was analysed.

The action of sodium hydrogen carbonate or acetate on trichloro-

benzenediazoniumsulphonic anhydride leads to the formation of *sodium dichlorodiazophenolsulphonate*, which, when treated with cuprous chloride in hydrochloric acid solution, yields *trichlorophenolsulphonic acid*. This crystallises in slender, white needles; the *sodium* salt, $C_6H_2O_4Cl_3SNa \cdot 1\frac{1}{2}H_2O$, forms white needles; the *barium* salt is only sparingly soluble.

When "coupled" with β -naphthol in alkaline solution, sodium dichlorodiazophenolsulphonate forms a violet *disodium* salt, which on treatment with dilute hydrochloric acid yields the *monosodium* salt, $OH \cdot C_6HCl_2(SO_3Na) \cdot N:N \cdot C_{10}H_6 \cdot OH$; this crystallises in glistening, brown needles, dissolves in water to form a violet solution, gives a violet coloration with alkali hydroxides or concentrated sulphuric acid, and on reduction yields 3:6-dichloro-2-aminophenol-4-sulphonic acid (Julius, *Chem. Zeit.*, 1903, 27, 846). The azo-compound dyes wool brownish-red, becoming violet-brown when treated with an alkali hydroxide; on treatment with potassium dichromate and sulphuric acid, there is obtained a violet colour, fast to alkali hydroxides. When treated with copper sulphate, the dyed wool becomes carmine-red.

The *azo-dye*, $SO_3Na \cdot C_6HBr_3 \cdot N:N \cdot C_{10}H_6 \cdot OH$, obtained by "coupling" diazotised 2:4:6-tribromoaniline-3-sulphonic acid with β -naphthol in alkaline solution, forms a carmine-red solution in concentrated sulphuric acid, dyes shades which are stable towards alkali hydroxides, and when treated with sodium hydrogen carbonate yields a *product* in which a bromine atom is substituted by a hydroxyl group. When "coupled" with β -naphthol, this forms the *azo-dye*,



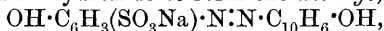
which crystallises in glistening, brown needles, dissolves in water to form a violet-red, in aqueous alkali hydroxides to form a violet, solution containing the *disodium* salt, and gives a bluish-violet coloration with concentrated sulphuric acid. It dyes wool a red shade, which changes to dark violet, and becomes fast to alkali hydroxides when treated with chromic acid.

When "coupled" with β -naphthol, the diazonium anhydride obtained from 2:5-dichloroaniline-4-sulphonic acid (Noelting and Kopp, *Abstr.*, 1905, i, 873) forms the *azo-dye*, $SO_3Na \cdot C_6H_2Cl_2 \cdot N:N \cdot C_{10}H_6 \cdot OH$, which crystallises in red needles and in its properties resembles Orange II. When treated with sodium hydrogen carbonate, the diazonium anhydride is converted into the corresponding *o*-hydroxy-compound only to the extent of 40 per cent.; when coupled with β -naphthol, the resulting mixture of diazo-compounds yields a red *product* which has the properties of an *o*-hydroxyazo-compound.

o-Chloroaniline-*p*-sulphonic acid is formed by heating *o*-chloroaniline hydrogen sulphate at 160° under 20–30 mm. pressure. The *sodium* salt, $(4H_2O)$, crystallises in needles and is only sparingly soluble in water. When treated with bromine, it forms 2-chloro-4:6-dibromoaniline, melting at 103° (m. p. 93.5°; Fittig and Buchner, *Abstr.*, 1878, 50). When diazotised and "coupled" with β -naphthol, *o*-chloroaniline-*p*-sulphonic acid yields an *azo-dye* resembling Orange II. The action of sodium hydrogen carbonate on the diazonium anhydride leads to substitution of only 25 per cent. of the chlorine by hydroxyl; on "coupling" the resulting mixture, a *product* is obtained which

dyes dirty-yellow shades, is only slightly altered by treatment with chromic acid, and does not exhibit the properties of an *o*-aminophenol derivative.

The β -naphthol dye, $\text{SO}_3\text{Na}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{N}\cdot\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}\cdot\text{H}_2\text{O}$, obtained from the diazonium anhydride of *o*-nitraniline-*p*-sulphonic acid (Nietzki and Lerch, Abstr., 1889, 144), crystallises in red needles, dyes wool a redder tone than does Orange II, and is stable towards alkali hydroxides. The diazonium anhydride dissolves in aqueous sodium hydrogen carbonate below 40° , with evolution of carbon dioxide and formation of *sodium diazophenolsulphonate*. The solution "couples" with β -naphthol in presence of sodium hydroxide to form the *azo-dye*,



which crystallises in glistening, black needles and dissolves in concentrated sulphuric acid to a bluish-violet solution. G. Y.

Diazo-derivatives of Diamines (Phenylenediamines, Benzidine). LÉO VIGNON (*Compt. rend.*, 1906, 142, 159—161).—A solution of diazobenzene chloride is decomposed by *o*- or *p*-phenylenediamine, and with *m*-phenylenediamine yields chrysoidine. Diazotised benzidine combines readily with amines and phenols to form stable derivatives.

The author attributes this difference in the behaviour of the two types of diamines to the fact that in the former the two amino-groups are attached to the same benzene nucleus and either cannot be diazotised, as in the case of the ortho-compound, or yield very unstable diazo-compounds, as in the case of the meta- and para-compounds; whilst in the latter, the two amino-groups, being attached to different benzene nuclei, are diazotised as readily as the monoamines.

M. A. W.

The Combination of more than One Molecule of a Diazo- or Tetrazo-compound in the production of Azo-dyes. WILHELM VAUBEL and OTTO SCHEUER (*Zeit. Farb.-Ind.*, 1906, 5, 1—2).—In the preparation of benzidine-blue from tetrazodiphenyl and R-salt, an excess of tetrazodiphenyl converts the dye into a substance insoluble in water and aqueous alkalis. The product seems to contain tetrazodiphenyl and R-salt in the ratio $3\text{C}_{12}\text{H}_8\text{N}_4\cdot\text{OH}\cdot\text{C}_{10}\text{H}_5(\text{SO}_3\text{Na})_2$; the original sulphonic groups appear to be present, but diazo- or diazoxy-groups cannot be detected. W. A. D.

Properties of Columbin, an Albumin from the White of Pigeons' Eggs. ALEXEI A. PANORMOFF (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 915—923. Compare Abstr., 1900, i, 709).—In addition to columbinin (*loc. cit.*), the author has separated from the white of pigeons' eggs another albumin, *columbin*, which has the composition: C, 52.47; H, 7.16; N, 14.82 per cent. These two albumins occur in equal proportions in the white of pigeons' eggs. Columbin is unstable and gives acid aqueous solutions, from which it is precipitated by alcohol, a solution of mercuric iodide in potassium iodide, or ammoniacal lead acetate solution. It has $[\alpha]_D - 36.33^\circ$ at 20° . *Columbin hydrochloride* has $[\alpha]_D - 67.21^\circ$ in aqueous solution, or -87.27° after being

heated at 100° for some time; on analysis, it gives the following numbers: C, 50.67; H, 6.87; N, 14.03; Cl, 2.85; S, 1.34 per cent.

The *hydrobromide* has $[\alpha]_D - 87.39^\circ$ after heating in solution at 100°; its composition was determined. T. H. P.

Properties of Albumins found in the White of Ducks' Eggs. ALEXEI A. PANORMOFF (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 923—930).—The white of ducks' eggs contains only two albumins, to which the names *anatinin* and *anatin* are given; these occur in the proportion of two parts of the former to one of the latter.

Anatin is precipitable by dilute ammonium sulphate solution, has $[\alpha]_D - 81.95^\circ$ at 20°, and yields the following numbers on analysis: C, 50.32; H, 6.84; N, 14.64; S, 2.96. The hydrochloride has $[\alpha]_D - 77.2^\circ$ at 20° in freshly-prepared solutions or $- 80.71^\circ$ in solutions previously heated at 100°.

Anatinin is precipitated by concentrated ammonium sulphate solution, has $[\alpha]_D - 37.09^\circ$ at 20°, and has the composition: C, 52.15; H, 7.30; N, 14.92; S, 2.01 per cent. Its hydrochloride has $[\alpha]_D - 39.22^\circ$ at 20°. T. H. P.

Albumin from the Blood-serum of the Cow. STEPHAN MAXIMOWITSCH (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 931—940).—By fractional precipitation of serum from defibrinated cows' blood with ammonium sulphate, the author has obtained an albumin which has the formula $C_{357}H_{552}O_{123}N_{93}S_3$ and $[\alpha]_D - 48.36^\circ$ at 20°, and resembles the albumin separated from the serum of horses' blood (*Abstr.*, 1902, i, 66). The *hydrochloride*, Alb., 7HCl, has $[\alpha]_D - 77.75^\circ$ at 20° in freshly-prepared solutions and $- 84.05^\circ$ after heating at 100°. The *phosphate*, Alb., 3H₃PO₄, has $[\alpha]_D - 71.38^\circ$ at 20° or $- 82.52^\circ$ after heating at 100°. T. H. P.

Precipitation of Serum-globulin from Blood-serum by means of Acetic Acid. WILLEM HUISKAMP (*Zeit. physiol. Chem.*, 1905, 46, 394—400).—The proteid precipitated by the addition of dilute acetic acid to diluted serum appears to be the same substance as that obtained by Hammarsten as a precipitate when 0.3 per cent. of sodium chloride is added. The reactions and elementary composition of the two are identical. It is further identical with serum-globulin. It is precipitated almost entirely by one-third saturation with ammonium sulphate and therefore consists chiefly of euglobulin. W. D. H.

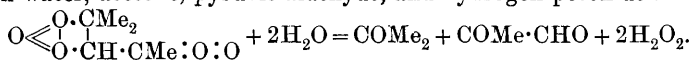
Animal Gelatins. IV. WL. S. SADIKOFF (*Zeit. physiol. Chem.*, 1905, 46, 387—393. Compare *Abstr.*, 1904, i, 462).—Gelatins or glutins differ in many of their solubilities from gluteins or cartilage-glutins. By means of saline solutions, gelatin is divisible into (1) a part which is insoluble in salt solution, (2) a part soluble in salt solution but precipitated by acid, and (3) a part soluble in both salt solution and acids. W. D. H.

Organic Chemistry.

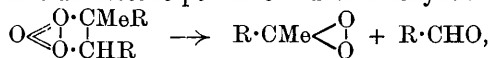
Preparation of Methane. HERBERT S. ELWORTHY and ERNEST H. WILLIAMSON (D.R.-P. 161666).—A gas, consisting principally of methane, may be prepared by passing a mixture of carbon monoxide (1 vol.) and hydrogen (3 vols.) over finely-divided nickel at 250°. The mixture is obtained by adding the necessary quantity of hydrogen, preferably prepared by the action of steam on heated iron, to water-gas which has been freed from carbon dioxide. A suitable apparatus is described and illustrated. C. H. D.

Action of Ozone on Organic Compounds. CARL D. HARRIES (*Annalen*, 1905, 343, 311—375).—A *résumé* of the earlier work on the action of ozone on the organic compounds is given. Hydrocarbons, such as methane and ethylene, are attacked and also alcohols, in which case aldehydes, acids, and hydrogen peroxide are formed. Occasionally explosive peroxides of unknown constitution have been obtained.

In a long series of papers (Abstr., 1903, i, 605; 1904, i, 413; 1905, i, 15, 361, 757, 861) it has been shown that unsaturated hydrocarbons and unsaturated alcohols combine with one molecule of ozone to form ozonides, whilst unsaturated ketones, aldehydes, and monobasic acids combine with four atoms of oxygen, one molecule of ozone combining at the ethylene linking, and the fourth atom of oxygen with the carbonyl group. The constitution of the ozonides is demonstrated by their reaction with water, thus: the ozonide of mesityl oxide yields, with water, acetone, pyruvic aldehyde, and hydrogen peroxide:



Methylheptenone yields with ozone an ozonide which decomposes immediately into an acetone peroxide and an aldehyde:



no hydrogen peroxide being formed. On the other hand, mesityl oxide and methylheptenoneozonide both yield with water hydrogen peroxide. It follows, therefore, that the hydrogen peroxide arises from the oxygen atom linked to the carbonyl group. It should be noted that the group $\text{R} \cdot \text{CMe} \cdot \text{C} <$ always yields with ozone an acetone peroxide.

Generally it can be said that ozone acts on organic compounds in two ways: (1) forming an ozonide, when the ozone attaches itself to an unsaturated carbon linking, and (2) when the ozone molecule is decomposed, labile peroxides of the carbonyl group being formed.

The formation of triozonides of benzene is in favour of the Kekulé formula of benzene, but opposed to the centric formula. Similarly, diphenyl yields a *tetraozonide*, facts which indicate the presence of ethylene linkings resembling those of the aliphatic series. Naphthalene yields a *diozonide* only, from which it can be concluded that

the linkings in the two naphthalene nuclei are different. It appears, in consequence, that a centric structure is inactive to ozone.

[With KURT LANGHELD.]—The ozonides were prepared by passing ozone through the dried substance, a process which must be carried on for about two hours for each three grams of ozonide produced; the ozonide is purified by dissolving it in ethyl acetate and precipitating by light petroleum.

The *ozonide* of allyl alcohol, $O_3 \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH} \cdot \text{CH}_2 \cdot \text{OH} \end{smallmatrix}$, is a syrup decomposing at the ordinary temperature and yielding an aldehyde when boiled with water; when distilled under reduced pressure, it decomposes in a similar manner. The *ozonide* of secondary methylheptenol, $O_3 \begin{smallmatrix} \text{CMe}_2 \\ | \\ \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{OH} \end{smallmatrix}$, is an oil having a sp. gr. 1.0992 at 25.5°. Tertiary methylhexenol is prepared from allylacetone and magnesium methiodide, and is a liquid boiling at 57° under 16 mm. pressure. The *ozonide*, $O_3 \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{OH} \end{smallmatrix}$, is a liquid having a sp. gr. 1.0703 at 23.5°. The *ozonide* of tertiary dimethylheptenol, $O_3 \begin{smallmatrix} \text{CMe}_2 \\ | \\ \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{OH} \end{smallmatrix}$, has a sp. gr. 1.0603 at 23.5°, and is decomposed by water into acetone and an aldehyde. The *ozonide* of allylacetone, $O_3 \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{O} \cdot \text{O} \end{smallmatrix}$, is an explosive syrup with a sp. gr. 1.1814 at 19°, and is decomposed by boiling with water into formaldehyde, lævulinaldehyde, and hydrogen peroxide.

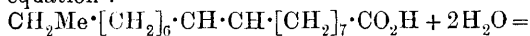
The treatment of methylheptenone with ozone leads to the formation of acetone peroxide. If the crude product of ozonisation is boiled with water, lævulinaldehyde is produced together with acetone peroxide.

The *ozonide* of citronellal, $C_{10}H_{18}O_5$, is a syrup having a sp. gr. 1.0746 at 21°; it decomposes on distillation into the aldehyde and oxygen, and appears when boiled with water to form a ketonealdehyde. The *ozonide* of citral, $C_{10}H_{16}O_5$, is a syrup having a sp. gr. 1.1486 at 21°, and is decomposed by warming with water. The two ozonides last mentioned possess molecular weights differing considerably from the unimolecular formulæ. The *ozonide* of isocrotonic acid,

$O_3 \begin{smallmatrix} \text{CHMe} \\ | \\ \text{CH} \cdot \text{C}(\text{OH}) \cdot \text{O} \cdot \text{O} \end{smallmatrix}$, is an extremely explosive syrup, which decomposes into oxygen and isocrotonic acid when kept. If a solution of isocrotonic acid in water is ozonised, acetaldehyde and glyoxylic acid are formed; hence, the constitution of the ozonide is determined. *Cenanthyl peroxide*, $\text{CH}_2\text{Me} \cdot [\text{CH}_2]_4 \cdot \text{CH} \cdot \text{O} \cdot \text{O}$, prepared from cenanthaldehyde is an oil having a sp. gr. 0.9081 and $n_D = 1.42876$ at 8°. It is decomposed by water into the aldehyde and hydrogen peroxide; it decomposes with development of heat into heptoic acid, a change which is accelerated by the presence of alkali; dilute acids bring about the evolution of oxygen.

[With CARL THIEME.]—Treatment with ozone has been used to

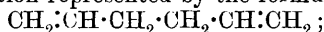
ascertain the relation of the isomerides, oleic and elaidic acids. The ozonides of both acids are decomposed by water according to the equation :



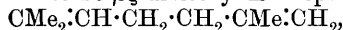
$\text{CH}_2\text{Me}\cdot[\text{CH}_2]_6\cdot\text{CHO} + \text{CHO}\cdot[\text{CH}_2]_7\cdot\text{CO}_2\text{H} + 2\text{H}_2\text{O}_2$,
an observation which is in agreement with the fact that both dibromo-oleic and dibromoelaidic acids yield the same stearolic acid. A solution of sodium oleate was ozonised and then evaporated under reduced pressure; nonylaldehyde and pelargonic acid, $\text{C}_8\text{H}_{17}\cdot\text{CO}_2\text{H}$, are extracted from the distillate by ether, and can be separated by distillation under a pressure of 15 mm. The residual alkaline liquor was acidified and extracted with ether, giving azelaic acid (m. p. 106°). The *semicarbazone* of nonylaldehyde, $\text{C}_9\text{H}_{18}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, crystallises in leaflets melting at 84° .

The ozonisation of elaidic acid could only be carried out in chloroform solution; the *ozonide* is a gelatinous mass which, when heated with water, gives hydrogen peroxide; it reduces Fehling's solution, oxidises potassium iodide, and decolorises indigo and potassium permanganate. The *ozonide* of oleic acid prepared in the same way has similar properties. The *calcium* salt of pelargonic acid is a powder melting at 216° ; the *silver* salt is sensitive to light. The half aldehyde of azelaic acid has been isolated in the form of the *semicarbazone*, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot[\text{CH}_2]_7\cdot\text{CO}_2\text{H}$, from the acidified alkaline liquor obtained in the ozonisation of sodium oleate; it melts at 163° .

[With HANS TÜRK.]—The constitution of several hydrocarbons has been elucidated by their reaction with ozone. Diallyl has been shown to have the constitution represented by the formula



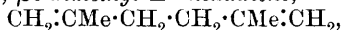
it is converted into a *diozonide*, $\text{C}_6\text{H}_{10}\text{O}_6$, by treatment with ozone in chloroform solution; the diozonide is an explosive syrup, which reacts with water giving a mixture of succinic acid and succinaldehyde. The hydrocarbon, C_9H_{16} , prepared by Harries and Weil (Abstr., 1904, i, 361), has been shown to be $\beta\zeta$ -dimethyl- $\Delta^{\beta\zeta}$ -heptadiene,



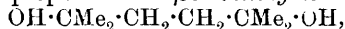
and not the $\Delta^{\beta\epsilon}$ -heptadiene; it was previously stated that its diozonide did not give lævulinaldehyde, but it is now found that the diozonide, $\text{C}_9\text{H}_{16}\text{O}_6$, yields the aldehyde on prolonged boiling with water. If the hydrocarbon is treated with ozone under water, it passes into solution; both hydrogen peroxide and an aldehyde can be detected in the solution, and on evaporating an explosive syrup is left, having

probably the constitution $\text{O}_3\begin{array}{c} \diagup \quad \diagdown \\ \text{CH}_2 \\ \text{CMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHO} \end{array}$.

The hydrocarbon, $\beta\epsilon$ -dimethyl- $\Delta^{\beta\epsilon}$ -hexadiene,



is an oil boiling at 137° under 755 mm. pressure; on repeated distillation, the boiling point falls to 115 — 117° . The *dibromide*, prepared by treatment with hydrogen bromide in acetic acid solution, melts at 71° . The hydrocarbon is prepared from $\beta\epsilon$ -dimethylhexane- $\beta\epsilon$ -diol,



which is obtained from magnesium methyl iodide and ethyl succinate and crystallises in leaflets melting at 89° . It is converted by hydrogen bromide in acetic acid solution into $\beta\epsilon$ -dimethylhexane- $\beta\epsilon$ -dibromide, $\text{CBrMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CBrMe}$, which melts at 71° and loses hydrogen bromide when exposed to the air. When boiled with pyridine, it yields a mixture, the main constituent of which is the hydrocarbon just described; at the same time, a solid hydrocarbon, C_8H_{14} , which melts at -5° and boils at 142° , is formed; it is readily oxidised by the air to a compound, $\text{C}_8\text{H}_{14}\text{O}_2$, and combines with hydrogen bromide, yielding an oil, $\text{C}_8\text{H}_{15}\text{Br}$, which combines with bromine and decolorises permanganate. $\beta\epsilon$ -Dimethyl- $\Delta^{\alpha\epsilon}$ -hexadiene yields a *diozonide*, $\text{C}_8\text{H}_{14}\text{O}_6$, which is a yellow, explosive liquid and decomposes on keeping, formaldehyde being produced. When the hydrocarbon is treated with ozone in the presence of water, formaldehyde, hydrogen peroxide, and acetonylacetone are produced. These facts are evidence for the constitution of the hydrocarbon.

[With VALENTIN WEISS.]—Renard's "ozotoluene," $\text{C}_7\text{H}_8\text{O}_6$ (*Compt. rend.*, 1895, 121, 651), prepared from toluene and ozone at 0° , appears to have the formula $\text{C}_7\text{H}_8\text{O}_7$ and to be a decomposition product of the triozonide, which is only formed at -21° and decomposes explosively at the ordinary temperature. On boiling the ozotoluene with water, methylglyoxal and glyoxal are formed. *m*-Xylenetriozonide is only formed at very low temperatures. *Mesitylenetriozonide*, $\text{C}_6\text{H}_3\text{Me}_3(\text{O}_3)_3$, is a gelatinous material which explodes at the ordinary temperature; it yields with water methylglyoxal, which can be isolated as a *disemicarbazone* (m. p. $255-257^{\circ}$).

Naphthalenediozonide is obtained as explosive crystals by passing ozone into a chloroform solution of naphthalene; when decomposed with water, phthalaldehyde and phthalic acid are formed.

The *diozonide* of phenanthrene, $\text{C}_{14}\text{H}_{10}\text{O}_6$, and the *tetraozonide* of diphenyl are explosive, crystalline substances.

Attempts have been made to prepare Berthelot's ethyl peroxide, Et_4O_8 ; ozone and carbon dioxide were passed into dry ether, the ether evaporated under reduced pressure, and the residue distilled under 20 mm. pressure at $40-50^{\circ}$. The colourless, viscid liquid deposited crystals at a very low temperature and exploded when air was admitted. The carbon was 15.28—25.65 per cent., and not 58.54 per cent., as Berthelot's formula requires.

K. J. P. O.

The Addition of Hydrogen Chloride to *iso*Butylene Oxide,

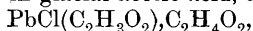
$\text{O} \begin{array}{c} \text{CMe}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array}$. LOUIS HENRY (*Compt. rend.*, 1906, 142, 493—497).—

*iso*Butylene oxide, obtained by the action of dry powdered potassium hydroxide on chlorotrimethyl carbinol, $\text{CH}_2\text{Cl} \cdot \text{CMe}_2 \cdot \text{OH}$ (prepared from magnesium methyl bromide, chloroacetone, and ethyl chloroacetate), combines readily with hydrogen chloride to form β -chloroisobutyl alcohol, $\text{CMe}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{OH}$, which is a thick, colourless liquid with an agreeable odour, boils at $132-133^{\circ}$, and does not solidify in a mixture of solid carbon dioxide and ether, and in this respect differs from its isomeride chlorotrimethylcarbinol (compare Krassusky, *Abstr.*, 1901, i, 246), which forms a crystalline solid melting at -20° . When heated

with hydrochloric acid at 60° , β -chloroisobutyl alcohol forms the ether, $(\text{CMe}_2\text{Cl}\cdot\text{CH}_2)_2\text{O}$, dissolves in a mixture of nitric and sulphuric acids to form the nitrate, $\text{CMe}_2\text{Cl}\cdot\text{CH}_2\cdot\text{NO}_3$, and reacts with nitrous acid to form the nitrite, $\text{CMe}_2\text{Cl}\cdot\text{CH}_2\cdot\text{O}\cdot\text{NO}$, whilst chlorotrimethylcarbinol yields $\alpha\beta$ -dichloroisobutane with hydrochloric acid and does not react with a mixture of nitric and sulphuric acids nor with nitrous acid.

M. A. W.

Reactions between Lead Chloride and Lead Acetate in Acetic Acid and Water Solutions. JOHN WHITE (*Amer. Chem. J.*, 1906, **35**, 217—227).—When lead chloride is dissolved in a hot solution of lead acetate in glacial acetic acid, a double salt,



is obtained, which forms monoclinic, prismatic crystals and, when left in the air, gradually loses a portion of its acid of crystallisation.

Carius (*Annalen*, 1863, **125**, 87) has shown that lead chloride dissolves in an aqueous solution of lead acetate to form a salt to which he assigned the formula $\text{PbCl}(\text{C}_2\text{H}_3\text{O}_2), \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2, 3\text{H}_2\text{O}$. It is now found that this salt crystallises in tufts of silky needles and has a composition which is represented by one of the formulæ, $\text{PbCl}(\text{C}_2\text{H}_3\text{O}_2), \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2, \text{H}_2\text{O}$; $\text{PbCl}(\text{C}_2\text{H}_3\text{O}_2), \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2, 2\text{H}_2\text{O}$; or $\text{PbCl}(\text{C}_2\text{H}_3\text{O}_2), \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2, \frac{1}{2}\text{C}_2\text{H}_4\text{O}_2$, between which it was not possible to decide. A determination of the molecular weight of this salt by the cryoscopic method, using water as the solvent, gave a value about one-fourth of that required by any of the proposed formulæ, indicating that dissociation had taken place; similar results were obtained with the double calcium salt, $\text{CaCl}(\text{C}_2\text{H}_3\text{O}_2), 5\text{H}_2\text{O}$, described by Fritsche (*Ann. Phys. Chem.*, 1833, **28**, 121).

The behaviour of lead chloride towards alkali acetates is different from that of lead iodide, the chloride undergoing double decomposition, whilst, as has been shown previously (*Abstr.*, 1904, i, 134), the iodide combines with them to form double salts.

E. G.

Reactions involved in the Formation of certain Complex Salts of Lead. JOHN WHITE and J. M. NELSON (*Amer. Chem. J.*, 1906, **35**, 227—235).—Experiments have been made with the object of preparing the salt $\text{PbI}\cdot\text{C}_2\text{H}_3\text{O}_2$, but without success. When lead acetate is heated with methyl iodide and a mixture of acetic acid and acetic anhydride, the double salt, $5\text{PbI}\cdot\text{C}_2\text{H}_3\text{O}_2, \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, is obtained, which forms monoclinic crystals. It has been found that in order to prevent the formation of lead iodide in the preparation of this salt, the temperature should not be allowed to exceed 70 — 75° , and that certain conditions of concentration and relative proportions of the reacting substances must be observed. The results of the experiments indicate that the salt $\text{PbI}\cdot\text{C}_2\text{H}_3\text{O}_2$ is formed as an intermediate compound.

E. G.

Nitration in the Presence of Phosphoric Oxide. ROBERT BEHREND and HANS OSTEN (*Annalen*, 1905, **343**, 152—155).—A mixture of fuming nitric acid and phosphoric oxide has been tried as a nitrating mixture; generally it is not to be preferred to the

ordinary methods. Ethyl acetoacetate yields the peroxide of ethyl diisonitrososuccinate. Similarly, nitrotartaric acid and tartronic acid can be easily prepared when tartaric acid is treated with a mixture of nitric acid and the phosphoric oxide; the first-mentioned acid is produced immediately, whilst the tartronic acid is formed when the mixture is kept for two weeks. Nitrohydantoin can be easily prepared from hydantoin.

K. J. P. O.

Synthesis of Derivatives of Ethyl Acetoacetate. II.

MILORAD Z. JOVITSCHITSCH (*Ber.*, 1906, **39**, 784—788. Compare *Abstr.*, 1902, i, 202).—The action of nitric acid (1 mol.) of sp. gr. 1.15 on ethyl isonitrosoacetoacetate leads to the formation of the nitrolic acid of ethyl acetate, which, when shaken with an excess of hydrochloric acid of sp. gr. 1.2, yields ethyl chloro-oximinoacetate. The nitrolic acid and the chloro-oximinoacetate are obtained in almost quantitative yields. The action of chlorine on the nitrolic acid of ethyl acetate in aqueous or ethereal solution leads to the formation of a number of products, amongst which are ethyl chloro-oximinoacetate and the oily peroxide of ethyl diisonitrososuccinate, whilst on further treatment with chlorine, the chloro-oximinoacetate is decomposed.

Ethyl bromo-oximinoacetate, $\text{OH}\cdot\text{N}\cdot\text{CBr}\cdot\text{CO}_2\text{Et}$, formed by the action of bromine on the nitrolic acid or on ethyl chloro-oximinoacetate, crystallises in small, snow-white needles, has a burning taste, melts at $85-86^\circ$, and is readily soluble in ether or benzene, but only sparingly so in light petroleum or water. It interacts with aniline, forming ethyl isonitrosoanilinoacetate, and yields hydroxylamine when boiled with dilute hydrochloric acid.

G. Y.

Dehydration of Hydroxy- β -alkylpivalic Esters. ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, [iii], **35**, 111—133).—When ethyl hydroxymethylpivalate [ethyl β -hydroxy- $\alpha\alpha$ -dimethylbutyrate] is prepared by Bouveault's method (*Abstr.*, 1900, i, 131), there is also formed some ethyl hydroxypropenylpivalate, $\text{CHMe}\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ (Jaworsky, *Abstr.*, 1903, i, 729), in addition to the diethyl pentamethylglutarate observed by Bouveault (*loc. cit.*).

β -Hydroxy- $\alpha\alpha$ -dimethylbutyric acid, $\text{OH}\cdot\text{CHMe}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$, prepared by saponifying the ethyl ester with potassium hydroxide in alcohol, forms a crystalline, hygroscopic mass, melts at 31° , and boils at 148° under 15 mm. pressure. When heated with benzylamine at 180° , no benzylamide is formed; the *benzylamine* salt melts at 71° . The *acetyl* derivative, obtained by the action of acetyl chloride on the acid, separates from light petroleum in large crystals, melts at 58° , and boils at 147° under 12 mm. pressure. The *phenylcarbamate* crystallises from a mixture of ether and light petroleum and melts at 129° . When the acid is heated with excess of hydriodic acid, it is converted into β -iodo- $\alpha\alpha$ -dimethylbutyric acid, which crystallises from light petroleum and melts at 44° .

Ethyl β -hydroxy- $\alpha\alpha$ -dimethylbutyrate is a viscous liquid and boils at 91° under 13 mm. pressure (compare Bouveault, *loc. cit.*), the *acetyl* derivative is viscous and boils at 110° under 24 mm. pressure. The *phenylcarbamate* crystallises from a mixture of ether and light petrol-

eum in colourless needles and melts at 86° . When the ester, dissolved in benzene, is treated with phosphoric oxide, it undergoes dehydration, furnishing ethyl $\alpha\alpha$ -dimethylisocrotonate, $\text{CH}_2\text{:CH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$, which boils at $141\text{--}142^{\circ}$ and on hydrolysis with potassium hydroxide in alcohol furnishes the *acid*. This is a colourless, mobile liquid, which boils at 99° under 23 mm. pressure and at 185° under atmospheric pressure, and has a sp. gr. 0.9567 at 15° . It solidifies when cooled and then melts at -6° . The *zinc, copper, calcium, barium, and lithium* salts were prepared. The *chloride* is a liquid of pungent odour, which boils at 26° under 14 mm. pressure. The *phenylhydrazide* crystallises from ether and melts at 98° , the *anilide* separates from a mixture of ether and light petroleum in large crystals and melts at 83° , and the *amide*, obtained by saturating the chloride with dry ammonia, forms small, white crystals, melts at 93° , and is very soluble in ether, alcohol, or water.

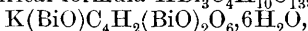
When $\alpha\alpha$ -dimethylisocrotonic acid is treated with bromine in chloroform solution, it is converted into $\beta\gamma$ -dibromo- $\alpha\alpha$ -dimethylbutyric acid, which crystallises from a mixture of ether and light petroleum in groups of slender needles and melts at 90° .

On reduction with sodium, $\alpha\alpha$ -dimethylisocrotonic acid yields the corresponding *dimethylbutenol*, $\text{CH}_2\text{:CH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$. This is a mobile, almost odourless liquid boiling at $130\text{--}131^{\circ}$. The *acetate* is a liquid of pleasant odour and boils at 149° . The *phenylcarbamate* crystallises from light petroleum in long needles and melts at $68\text{--}69^{\circ}$.

$\alpha\alpha$ -Dimethylisocrotonic acid combines with one mol. of hydrogen iodide to form the β -iodo- $\alpha\alpha$ -dimethylbutyric acid described above, and on oxidation with potassium permanganate in presence of potassium hydrogen carbonate yields dimethylmalonic acid. T. A. H.

Simple and Complex Salts of Bismuth. ARTHUR ROSENHEIM and WALTER VOGELSANG (*Zeit. anorg. Chem.*, 1906, **43**, 205—216).—[With M. Koss.]—When bismuth nitrate, dissolved in nitric acid, is treated with three molecular equivalents of tartaric acid, the compound $\text{Bi}(\text{C}_4\text{H}_4\text{O}_6)\text{NO}_3\cdot 5\text{H}_2\text{O}$ separates in colourless, prismatic crystals. On dissolving this salt in a concentrated boiling solution of tartaric acid and allowing to cool, the compound $\text{BiH}(\text{C}_4\text{H}_4\text{O}_6)_2\cdot 2\text{H}_2\text{O}$ is obtained in lustrous needles. Both compounds are decomposed by water with formation of basic salts. Contrary to the statements of Baudran (*Abstr.*, 1900, i, 375) and others, salts corresponding with antimony potassium tartrate could not be obtained.

From the solution of the salt last mentioned in excess of alkali, a compound of the empirical formula $\text{KBi}_3\text{C}_4\text{H}_{10}\text{O}_{13}$, perhaps



separates in small crystals soluble without decomposition in water; the same compound is also obtained by other methods. Its aqueous solution is strongly dextrorotatory, but with increasing amounts of alkali the rotation diminishes and finally changes sign. From a nitric acid solution of bismuth nitrate to which excess of alkali had been added, a second compound, $\text{K}_2\text{BiC}_4\text{H}_3\text{O}_7$, was obtained in lustrous scales. From observations of the effect on polarised light of tartaric acid solutions to which varying amounts of bismuth nitrate and sodium

hydroxide had been added, the conclusion is drawn that other complex salts besides those of the above type exist. Complex sodium salts have not been obtained in crystalline form, but an ammonium salt, $\text{NH}_4\text{BiC}_4\text{H}_2\text{O}_6$, has been isolated in the form of microscopic prisms.

From a solution of thiocyanic acid saturated with bismuth carbonate, the compound $\text{Bi}(\text{SCN})_2 \cdot \text{OH} \cdot 5\text{H}_2\text{O}$ separates in glistening plates on addition of alcohol. When excess of the acid is added and the solution concentrated, normal *bismuth thiocyanate*, $\text{Bi}(\text{SCN})_3 \cdot 14\text{H}_2\text{O}$, is obtained in deep red, transparent needles. When potassium thiocyanate is added to the same solution, the compound $\text{K}_3\text{Bi}(\text{SCN})_6$, already described by Vanino and Hauser (Abstr., 1902, i, 14), separates. On the other hand, the compound $\text{K}_9\text{Bi}(\text{SCN})_{12}$, described by these authors, could not be obtained and probably does not exist.

Normal *bismuth acetate*, $\text{Bi}(\text{C}_2\text{H}_3\text{O}_2)_3$, recently described by Colonna (Abstr., 1905, i, 852), has been obtained by boiling the carbonate with glacial acetic acid in the presence of mannitol. G. S.

Thioglycollic Acid. PETER KLASON and TOR CARLSON (*Ber.*, 1906, 39, 732—738).—The yield of thioglycollic acid from the action of potassium hydrosulphide on chloroacetic acid is better the more water is present. When thioglycollic acid is heated under diminished pressure, various condensation products are formed according to the conditions; in one case, a compound crystallising from benzene as a snow-white powder, melting at about 80° , and giving numbers on analysis corresponding with those for *thioglycollide*, $\text{S} \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CO} \end{smallmatrix}$, was obtained.

Determinations of the electrical conductivity of thioglycollic acid gave $K = 0.0291$, a value at variance with that obtained by Ostwald, who found $K = 0.0225$.

Ethyl thioglycollate boils at 55° under 17 mm. pressure.

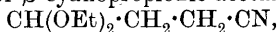
Thioglycollamide crystallises in white needles, melts at 52° , and is oxidised to dithioglycollamide on exposure to air.

Barium thioglycollate, $\text{Ba}(\text{S} \cdot \text{CH}_2 \cdot \text{CO}_2)_2 \cdot \text{Ba} \cdot 3\text{H}_2\text{O}$, crystallises in glistening plates; 0.85 part dissolves in 100 parts of water at 17° . The *antimony*

salt, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{S} \cdot \text{Sb} \begin{smallmatrix} \text{S} \cdot \text{CH}_2 \\ | \\ \text{O} \cdot \text{CO} \end{smallmatrix}$, prepared by the addition of thioglycollic acid (3 mols.) to a solution of antimony chloride (1 mol.) in dilute hydrochloric acid, forms white, monoclinic crystals. The *arsenic* derivative, $\text{As}(\text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H})_3$, forms rhombic crystals. The *platinum* derivative, $\text{Pt}(\text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H})_2$, is a red solid. A. McK.

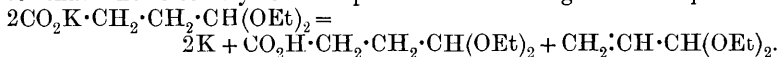
Preparation of Aliphatic Dialdehydes. ALFRED WOHL and H. SCHWEITZER (*Ber.*, 1906, 39, 890—897).—The authors describe an electrolytic method for the preparation of aliphatic dialdehydes. Potassium β -diethoxypropionate was electrolysed by Crum Brown and Walker's method with a current of 3 amperes and an *E.M.F.* of 8—10 volts, the change represented by the equation occurring: $2\text{KO} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2 = 2\text{K} + 2\text{CO}_2 + \text{C}_2\text{H}_4[\text{CH}(\text{OEt})_2]_2$. The resulting succintetraethylacetal was proved to be identical with Harries' compound (Abstr., 1902, i, 345).

Potassium γ-diethoxybutyrate, $\text{CH}(\text{OEt})_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{K}$, prepared by the saponification of β-cyanopropionic acetal,



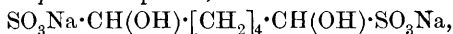
is an amorphous, hygroscopic mass.

Ethyl γ-diethoxybutyrate, $\text{CH}(\text{OEt})_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, prepared by the action of ethyl iodide on the potassium salt, is an oil which boils at 113—114° under 10 mm. pressure. When the potassium salt was electrolysed, the double acetal of adipic aldehyde was formed in a 35 per cent. yield. Acraldehyde acetal was, however, also produced, so that the electrolysis also proceeded according to the equation:



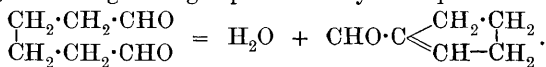
Adipic dialdehyde tetra-acetal, $\text{CH}(\text{OEt})_2 \cdot [\text{CH}_2]_4 \cdot \text{CH}(\text{OEt})_2$, is a colourless oil which boils at 148° under 10 mm. pressure.

Adipic dialdehyde (hexane-αζ-dial), prepared by the action of dilute sulphuric acid on the acetal, boils at 92—94° under 9 mm. pressure. Determinations of its molecular weight by the cryoscopic method indicated that the aldehyde is associated in benzene solution, whereas in aqueous solution it is unimolecular. The residue remaining in the distilling flask after the aldehyde had been distilled off boiled mainly at 130° under 0.2 mm. pressure and was apparently a polymeric form of the aldehyde. Adipic dialdehyde is remarkably stable. When sealed in a glass tube, it may be kept for weeks before it assumes a syrupy consistency; in this respect it differs from octanedial and from succindialdehyde. Adipic dialdehyde is readily resinified when gently warmed with aqueous alkalis. When a solution of nitrophenylhydrazine in acetic acid is added to a solution of adipic dialdehyde in ethyl alcohol, the *bisnitrophenylhydrazone*, $\text{C}_{18}\text{H}_{20}\text{O}_4\text{N}_6$, separates in brick-red crystals which melt at 169—170° (corr.). The *disemicarbazone*, $\text{C}_8\text{H}_{16}\text{O}_2\text{N}_6$, crystallises in prisms and melts at 206° (corr.). The *dioxime*, $\text{C}_6\text{H}_{12}\text{O}_2\text{N}_2$, separates from water in needles and melts at 185—186° (corr.). The *bisulphite* compound,



crystallises in prisms.

When adipic dialdehyde is heated with water for five hours at 110°, it forms *cyclopentenealdehyde*, which was identified by its semicarbazone, the change being represented by the equation



A. McK.

Action of Acetone on Alkali Sulphites. VICTOR ROTHMUND (*Monatsh.*, 1905, 26, 1545—1558. Compare Lumière, Lumière, and Seyewetz, *Abstr.*, 1897, ii, 470; Kerp, *Abstr.*, 1904, i, 713).—The formation of compounds of acetone with sulphurous acid, alkali sulphites, or alkali hydrogen sulphites in aqueous solution is confirmed by means of conductivity measurements and cryoscopic molecular weight determinations. The formation of the compound of acetone and sulphurous acid is represented by the equation: $\text{SO}_3 + \text{C}_3\text{H}_6\text{O} + \text{H}_2\text{O} =$

$\text{SO}_3\text{H}(\text{C}_3\text{H}_6\text{O}) + \text{OH}$. Acetonesulphurous acid is a stronger acid than sulphurous acid, as is shown by the increase in the conductivity of aqueous sulphurous acid which ensues on addition of acetone; the formation of the acetonesulphurous acid takes place slowly, the maximum conductivity being reached in about an hour.

As sulphurous acid is dibasic towards phenolphthalein, but acetone-sulphurous, although a stronger acid, is monobasic, a solution of an alkali sulphite, neutral to phenolphthalein, becomes alkaline on addition of acetone.

G. Y.

Ketens. II. Dimethylketen. HERMANN STAUDINGER and HELMUT W. KLEVER (*Ber.*, 1906, 39, 968—971. Compare Abstr., 1905, i, 444).—The action of zinc on an ethereal solution of α -bromo-isobutyryl bromide leads to the formation of *dimethylketen*, $\text{CMe}_2\text{:CO}$, in 38 per cent. yield, which, however, cannot be separated from the solvent by fractional distillation. The use of less volatile solvents is inadmissible, as either the reaction does not take place or the keten produced polymerises. A 28 per cent. yield of the keten is obtained when ethyl acetate is employed as the solvent. To separate the pure keten, the mixed liquids are distilled at -20° under 15—16 mm. pressure, the distillate being collected in a flask at -80° ; under these conditions, ethyl acetate is very slightly volatile, and dimethylketen is obtained as a mobile, yellow liquid which is stable at -20° under atmospheric pressure. At the ordinary temperature, it polymerises to a colourless *substance*, which melts at 112 — 112.5° and appears to be identical with Wedekind and Weisswange's diketone, $(\text{CMe}_2\text{:CO})_2$. Dimethylketen, which is comparatively stable when dissolved in ether or ethyl acetate, is at once converted by oxygen into a white explosive powder, which is possibly a peroxide. The keten is converted by water or alcohol into isobutyric acid and its ester respectively; with aniline, it forms the anilide, and with phenylhydrazine the phenylhydrazide of isobutyric acid. With quinone, it forms a colourless additive *compound* which melts at 104.5° . The *compound* with quinoline melts at 152 — 153° and is stable to dilute acids, but by prolonged boiling with concentrated hydrochloric acid it is decomposed into quinoline and isobutyric acid.

C. S.

Formation of Formaldehyde during the Destruction of Sugar by Heating. AUGUSTE TRILLAT (*Zeit. Ver. deut. Zuckerind.*, 1906, 95—103. Compare Abstr., 1905, i, 325).—Formaldehyde is formed when sucrose is heated at 100° or any higher temperature, the amount increasing as the temperature rises. If the sucrose is heated in copper foil, it yields as much as 5.7 per cent. of the aldehyde, the increased amount obtained in this way being due to the catalytic action of the metal. The presence of air is not necessary for the formation of formaldehyde, small quantities of which are evolved when sucrose is heated either under oil or in an atmosphere of carbon dioxide.

On heating sugar to incipient carbonisation, it yields the following gaseous products: (1) 0.2—5.7 per cent. of formaldehyde; (2) acet-

aldehyde; (3) 0.5—1.4 per cent. of benzaldehyde; (4) 0.1—0.5 per cent. of acetone; (5) 0.1—0.5 per cent. of methyl alcohol; (6) 1—3 per cent. of acetic acid; (7) 1—3 per cent. of phenol derivatives.

Caramel, which is obtained by heating sugar with or without the addition of alkali, contains products of polymerisation of formaldehyde.

This formation of formaldehyde explains the disinfecting and deodorising action of the gases formed on burning sugar. T. H. P.

Presence of Formaldehyde in Caramelised Substances.

AUGUSTE TRILLAT (*Compt. rend.*, 1906, 142, 454—456. Compare *Abstr.*, 1905, i, 325).—When sugar is heated, formaldehyde occurs, not only in the gaseous products, but also in the residual caramel, the proportion increasing with the temperature at which the caramelisation is effected, as is shown in the following table:

	Temperature of caramelisation.	Formaldehyde in residue.	Formaldehyde liberated.
I.	125°	trace	trace
II.	150	0.090 per cent.	0.300 per cent.
III.	150—180	0.135 "	1.100 "
IV.	180—200	0.270 "	2.200 "

Out of five commercial samples of caramel examined three contained appreciable quantities of formaldehyde, 30, 45, and 325 mg. respectively per 100 grams of caramel.

The fermenting properties of sugar are much diminished by partial caramelisation, and caramel acts as an antiseptic or microbicide; the addition of 6 per cent. of sugar caramelised at 200° sterilised a solution of bouillon which had been inoculated with *Bacillus coli communis*, whilst the souring of milk containing the lactic acid ferment was prevented by the addition of 10 per cent. of the caramel.

M. A. W.

Inversion of Starch by Platinum Black. C. HUGH NEILSON (*Amer. J. Physiol.*, 1906, 15, 412—415).—Platinum black hydrolyses starch, and the sugar formed is probably maltose. The reaction is retarded by the products of hydrolysis. The higher the concentration of the starch solution, the slower the action of the platinum.

W. D. H.

Retrogression and Composition of Natural Starches other than Potato Starch. EUGÈNE ROUX (*Compt. rend.*, 1906, 142, 95—97).—Potato starch consists of amylose, which only differs from amylocellulose in its greater purity, and a substance to which the name "amylopectin" is given. The latter is dissolved by the action of malt, without production of sugars.

Starches from maize, wheat, rice, peas, and manioc all contain about the same amount of amylose, and they all contain amylopectin.

N. H. J. M.

Grignard's Reaction with Amino-acids. CARL PAAL and ERICH WEIDENKAFF (*Ber.*, 1906, 39, 810—813. Compare Abstr., 1905, i, 436; Süsskind, this vol., i, 133).—The action of magnesium ethyl iodide on ethyl diethylaminoacetate, prepared by the action of diethylamine on ethyl bromoacetate (compare Willstätter, Abstr., 1902, i, 266), leads to the formation of *diethylaminomethyl-diethylcarbinol*, $\text{NEt}_2 \cdot \text{CH}_2 \cdot \text{CET}_2 \cdot \text{OH}$, which is obtained as a colourless, viscid oil. It boils at 80—85° under 35 mm. or at 190° under the atmospheric pressure, slowly becomes yellow, is miscible with ether, alcohol, ethyl acetate, or benzene, and dissolves in hot water. It forms stable salts with mineral acids: the *hydrogen sulphate*, $\text{C}_{10}\text{H}_{23}\text{ON}, \text{H}_2\text{SO}_4$, crystallises in long, colourless needles and melts at 74—76°; the *platinichloride*, $(\text{C}_{10}\text{H}_{23}\text{ON})_2, \text{H}_2\text{PtCl}_6$, crystallises in stout, reddish-brown prisms and melts at 130—132°; the *aurichloride*, $\text{C}_{10}\text{H}_{21}\text{N}, \text{HAuCl}_4$, crystallises in slender, yellow needles and melts at 112—114°.

Diphenyldiethylaminomethylcarbinol, $\text{NEt}_2 \cdot \text{CH}_2 \cdot \text{CPh}_2 \cdot \text{OH}$, formed by the action of magnesium phenyl bromide on ethyl diethylaminoacetate, is obtained as a crystalline mass which melts at 47—49° and boils at 197° under 40 mm., or with partial decomposition at 280—300° under the atmospheric pressure. The *hydrochloride*, $\text{C}_{18}\text{H}_{23}\text{ON}, \text{HCl}$, forms white leaflets and melts at 166—167°; the *platinichloride*, $(\text{C}_{18}\text{H}_{23}\text{ON})_2, \text{H}_2\text{PtCl}_6$, crystallises in yellowish-red plates and melts at 185—186°; the *aurichloride*, $\text{C}_{18}\text{H}_{23}\text{ON}, \text{HAuCl}_4$, melts at 125—126°. G. Y.

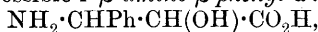
α -Dimethylaminobutyric Acid. EDOUARD DUVILLIER (*Bull. Soc. chim.*, 1906, [iii], 35, 156—159).—Dimethylamine reacts with α -bromobutyric acid at the atmospheric temperature to form *α -dimethylaminobutyric acid*, which separates, when its aqueous solution is evaporated under reduced pressure at the ordinary temperature over a desiccating agent, in crusts composed of small needles, is hygroscopic, and very soluble in alcohol. The *aurichloride* crystallises in lamellæ, is moderately soluble in water, very soluble in alcohol, and slightly so in ether. The *platinichloride* forms orange-red, monoclinic crystals and is very soluble in water or alcohol. The *hydrochloride* and the *cupric* salt were also prepared. The latter is a convenient means of obtaining the acid in a pure state. Approximate solubilities of the various salts in water or alcohol are given in the original.

T. A. H.

Glycinecarboxylic Acid. HERMANN LEUCHS (*Ber.*, 1906, 39, 857—861).—*Glycinecarboxylic anhydride*, $\begin{array}{c} \text{NH} \cdot \text{CO} \\ | \\ \text{CH}_2 \cdot \text{CO} \end{array} > \text{O}$, is obtained when carbethoxyglycyl chloride (Fischer and Otto, Abstr., 1903, i, 608) is heated under reduced pressure at 80—85° for one hour. It crystallises from ethyl acetate in short, six-sided prisms, has a bitter taste, and when heated at 100° evolves carbon dioxide. It dissolves fairly readily in ice-cold water, yielding an acid solution which begins to evolve carbon dioxide at 15°. It also evolves gas when rubbed with twice its weight of water at the ordinary temperature and yields an insoluble powder, $(\text{C}_2\text{H}_3\text{ON})_x$, with no definite melting point.

With alcoholic hydrogen chloride, the anhydride yields the ethyl glycine hydrochloride and with barium hydroxide solution, barium glycinecarboxylate (Siegfried, this vol., i, 144). J. J. S.

Isomeric Phenylserines. EMIL ERLÉNMEYER, jun. (and C. BARKOW) (*Ber.*, 1906, **39**, 791—794. Compare Erlenmeyer, *Abstr.*, 1893, i, 36, 166; 1899, i, 759; Erlenmeyer and Früstück, *Abstr.*, 1895, i, 281).—The second possible *r*- β -amino- β -phenyl- α -lactic acid,



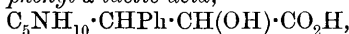
is formed together with small quantities of *r*- α -amino- β -phenyl- β -lactic acid, melting at 187—188°, by the action of ammonia in the cold on sodium oxyphenylacrylate obtained from solid chlorophenyl-lactic or bromophenyl-lactic acid. It crystallises in needles, decomposes at 241°, is only sparingly soluble in water, and forms a deep blue *copper* salt which is almost insoluble in water.

When heated with ammonia, sodium oxyphenylacrylate yields only the *r*- β -amino- β -phenyl- α -lactic acid, melting at 220—221°.

The following derivatives of β -amino- β -phenyl- α -lactic acid are prepared by the action of primary amines on sodium oxyphenylacrylate; the active substances are derived from the *l*-sodium salt having $[\alpha]_D - 157.89^\circ$:

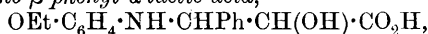
r- β -Anilino- β -phenyl- α -lactic acid, $\text{NHPh}\cdot\text{CHPh}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, prepared from the sparingly soluble sodium salt, crystallises in long, thin needles, melts at 156°, and is soluble in water, or, if prepared from the more soluble sodium phenyloxyacrylate, crystallises in nodules, melts at 158°, and is almost insoluble in water. The *l*-acid melts at 187° and has $[\alpha]_D - 20^\circ$; the *sodium* salt has $[\alpha]_D + 26.68^\circ$.

r- β -Piperidino- β -phenyl- α -lactic acid,



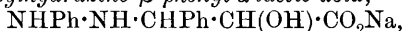
melts at 255°. The *d*-acid melts at 256° and has $[\alpha]_D + 43.9^\circ$.

r- β -Phenetidino- β -phenyl- α -lactic acid,



melts at 185°. The *l*-acid melts at 207° and has $[\alpha]_D - 35^\circ$; its *sodium* salt has $[\alpha]_D + 9.17^\circ$.

Sodium β -phenylhydrazino- β -phenyl- α -lactic acid,



yields on acidification the *anhydride*, $\text{NPh}\begin{matrix} \text{CO}-\text{CH}\cdot\text{OH} \\ \text{NH}\cdot\text{CHPh} \end{matrix}$, which melts at 174°; the optically active *sodium* salt has $[\alpha]_D - 197^\circ$, the *anhydride* $[\alpha]_D - 217^\circ$.

The optically active β -amino- β -phenyl- α -lactic acid, corresponding with the racemic acid melting at 241°, is amorphous; its deep blue *copper* salt has $[\alpha]_D + 21.8^\circ$. G. Y.

Carbethoxyl isoCyanate [Ethyl Carbinidecarboxylate]. OTTO DIELS and BERTRAM WOLF (*Ber.*, 1906, **39**, 686—688).—Ethyl nitrogentricarboxylate (*Abstr.*, 1903, i, 324) is converted into ethylene, carbon dioxide, water, and ethyl carbimidecarboxylate when heated with twice its weight of phosphoric oxide at 120°: $\text{N}(\text{CO}_2\text{Et})_3 = 2\text{C}_2\text{H}_4 + \text{CO}_2 + \text{H}_2\text{O} + \text{O}:\text{C}:\text{N}\cdot\text{CO}_2\text{Et}$. *Ethyl carbimidecarboxylate* is

collected in a receiver placed in a good freezing mixture and protected from atmospheric moisture. It is a colourless, mobile liquid with a characteristic odour, distils at 115—116° under 781 mm. pressure, and dissolves readily in acetone or ether. It readily reacts with water, yielding carbonyldiurethane (Folin, Abstr., 1897, i, 470), with ammonia yielding ethyl allophanate, and with ethyl alcohol yielding ethyl iminodicarboxylate. J. J. S.

Nitroacetamide. FLORIAN RATZ (*Monatsh.*, 1905, 26, 1487—1531. Compare Abstr., 1904, i, 298, 857).—The action of alcoholic ammonia on ethyl nitroacetate (Bouveault and Wahl, Abstr., 1904, i, 795), under cooling, leads to the formation of the *ammonium* salt of the ester, $C_4H_6O_4N \cdot NH_4$, which crystallises in slender, white needles, but by the action of an excess of aqueous or alcoholic ammonia the ester is converted into the ammonium salt of nitroacetamide, slowly at the laboratory temperature but more quickly at 100°. The ester interacts in the same way with methylamine or ethylamine, forming the corresponding alkylammonium salts of nitromethyl- or nitroethyl-acetamide; the *methylammonium* salt, $C_4H_{11}O_3N_3$, crystallises from chloroform and melts and decomposes at about 120°.

The action of ethyl iodide on silver nitroacetamide, suspended in acetone at about 5°, leads to the formation of:

(1) *Nitroethylacetamide*, $C_2H_3O_3N_2Et$, which is obtained in a yield not exceeding 30 per cent. of the theoretical; it crystallises in white needles, melts and decomposes at 114°, and is readily soluble in methyl alcohol, ethyl acetate, or acetone, but less so in ethyl alcohol, and only sparingly so in benzene or ether. Ebullioscopic molecular weight determinations show that in alcoholic solution the substance decomposes gradually and evolves a volatile product.

(2) Free nitroacetamide, which is obtained to the extent of 27 per cent. of the silver salt.

(3) An unstable *product*, which separates as a yellow syrup from the final mother liquors on evaporation or on addition of light petroleum.

Nitropropylacetamide, $C_2H_3O_3N_2Pr$, is formed by the action of propyl iodide on silver nitroacetamide to the extent of 32 per cent. of the theoretical; it crystallises in white needles and decomposes at 107°.

Nitroisoamylacetamide, $C_2H_3O_3N_2 \cdot C_5H_{11}$, is obtained in a yield of 28 per cent. of the theoretical; it forms glistening, fatty, white scales, melts and decomposes at 100—101°, and has a slight odour of fusel oil. On prolonged heating with water, alcohol, acetone, or other indifferent solvent, nitroethyl-, nitropropyl-, and nitroisoamyl-acetamides are decomposed, and, if the solution is distilled, the distillate gives a strong aldehyde reaction. When treated in the same way, nitromethylacetamide gives only a faint aldehyde reaction, but a strong odour of ethyl nitrate. The residue obtained on evaporating the solutions obtained from the ethyl, propyl, and isoamyl compounds contains two isomeric oximes:

(1) The *α-oxime*, $OH \cdot N : CH \cdot CO \cdot NH_2$, which is the more readily soluble in ethyl acetate, crystallises in white needles or nodular aggregates of needles, melts and evolves a gas at 129°, has a slight acid reaction in aqueous solution, and in moderately concentrated solutions

forms, with silver nitrate, the *additive* compound, $2\text{C}_2\text{H}_4\text{O}_2\text{N}_2\cdot\text{AgNO}_3$, crystallising in aggregates of slender, white needles. With silver nitrate in presence of 1 mol. of sodium ethoxide, the α -oxime forms the *silver* salt, $\text{C}_2\text{H}_3\text{O}_2\text{N}_2\text{Ag}$, which crystallises in nodular aggregates of small, stout, light grey needles. On prolonged heating with dilute acids, the α -oxime is hydrolysed with formation of 1 mol. each of ammonia, hydrogen cyanide, carbon dioxide, and water. The hydrolysis with dilute alkali hydroxides takes place more slowly but more completely, the hydrogen cyanide being partially hydrolysed. When heated at 100° with concentrated hydrochloric acid, the α -oxime yields carbon dioxide, ammonia, formic acid, and hydroxylamine. The α -oxime can be prepared by digesting ethyl isonitrosoacetate (Bouveault and Wahl, Abstr., 1904, i, 546) with alcoholic ammonia at 65 – 70° .

Alkyl derivatives of the α -oxime are prepared by shaking the silver derivative with the alkyl iodides in absolute methyl- or ethyl-alcoholic solution. They are colourless, crystalline substances and are more stable than the parent oxime, as is shown by the diminished rate of hydrolysis with dilute acids or alkali hydroxides.

The *methyl* derivative, $\text{C}_2\text{H}_5\text{O}_2\text{N}_2\text{Me}$, crystallises in needles and melts at 137.5 – 138.5° ; the *ethyl* derivative, $\text{C}_2\text{H}_5\text{O}_2\text{N}_2\text{Et}$, forms needles and melts at 125 – 125.5° ; the *propyl* derivative, $\text{C}_2\text{H}_5\text{O}_2\text{N}_2\text{Pr}$, crystallises in needles and melts at 99.5° ; the *amyl* derivative forms glistening, fatty scales and melts at 96° .

(2) The β -oxime, $\text{C}_2\text{H}_4\text{O}_2\text{N}_2$, which, in most solvents, is much less soluble than the α -oxime, crystallises in nodular aggregates, melts and decomposes at 119 – 120° , and does not form an insoluble additive compound with silver nitrate, but yields an explosive, yellow, amorphous *silver* salt, $\text{C}_2\text{H}_3\text{O}_2\text{N}_2\text{Ag}$, $\text{C}_2\text{H}_2\text{O}_2\text{N}_2\text{Ag}_2$ (?). The β -oxime is hydrolysed by concentrated hydrochloric acid in the same manner and with formation of the same products as the α -oxime, and is converted into the α -oxime when treated with ammonia.

When oxidised with potassium permanganate in sulphuric acid solution, the α - and β -oximes yield a *product*, $\text{O}_2(\text{N}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}_2)_2$ or $\text{NH}_2\cdot\text{CO}\cdot\text{CH}(\text{NO})\cdot\text{CH}(\text{NO})\cdot\text{CO}\cdot\text{NH}_2$, which forms a delicate, white, microcrystalline powder, decomposes, when rapidly heated, at 118 – 122° , and is insoluble in water or organic solvents, but dissolves in dilute alkali hydroxides, from its solution in which no precipitate separates on acidification.

Tables are given showing the comparative rates of hydrolysis, by means of dilute alkali hydroxides, of the two oximes and of nitroacetamide and its alkyl derivatives. The results show that the alkali hydroxide acts not only hydrolytically on the group $-\text{CO}\cdot\text{NH}_2$, but also as a cause of isomeric change. The auto-reduction which takes place in indifferent solvents is effective in alkaline solutions only at the commencement of the reaction.

With bromine water under cooling, nitroethylacetamide forms the *bromo*-derivative, $\text{C}_2\text{H}_2\text{O}_3\text{N}_2\text{BrEt}$, which is obtained as a fine, white powder, decomposes slowly at the ordinary temperature, or melts and decomposes when heated at 87 – 88° , and is readily soluble in chloroform or acetone, but less so in methyl or ethyl alcohol, and only sparingly so in water, ether, or benzene.

The author discusses the structure of the alkyl derivatives and the course of their formation by alkylation of nitroacetamide.

Pure bromonitroacetamide is prepared by adding slowly an alkaline alcoholic solution of potassium arsenite to an alcoholic solution of dibromonitroacetamide, treating the potassium derivative so formed with sulphuric acid, and extracting the product with ether. The aqueous solution of the potassium salt is colourless; the *lead* salt forms nodular aggregates of yellowish-white needles; the *silver* salt is obtained as a white, gelatinous precipitate which becomes crystalline.

Bromonitromalonamide and bromonitroacetamide interact in alcoholic solution, slowly at the laboratory temperature, or rapidly when heated, to form nitromalonamide and dibromonitroacetamide.

Nitroacetamide interacts with formaldehyde in 40 per cent. aqueous solution, in presence of ammonia, to form the product $(C_3H_5O_2N_2)_x$, which crystallises in microscopic, spherical aggregates and is insoluble in water, dilute acids, or the usual organic solvents, but dissolves in cold dilute alkali hydroxides or ammonia, from which it is reprecipitated unchanged on acidification. When heated with aqueous potassium hydroxide, it decomposes with evolution of ammonia. The white *silver*, *lead*, and *mercury*, green *copper*, and red *iron* salts are obtained as amorphous precipitates.

G. Y.

Action of Esters of certain Dibasic Acids on Magnesium Halogen Derivatives of Primary Aromatic Amines. F. BODROUX (*Compt. rend.*, 1906, 142, 401—402).—Ethyl oxalate reacts with the magnesium halogen derivative of a primary aromatic amine according to the equation: $C_2O_4Et_2 + 4RNH \cdot MgI = C_2(NHR)_4(OMgI)_2 + 2OEt \cdot MgI$. On treatment with dilute acid, a symmetrically substituted oxamide derivative is obtained, $C_2(NHR)_4(OMgI)_2 + 2HCl = MgCl_2 + MgI_2 + 2NH_2R + C_2O_2(NHR)_2$. In a similar manner, substituted amides are obtained from ethyl succinate, but not from ethyl malonate. The latter, in virtue of its methylenic hydrogen, simply displaces the aromatic amine from the magnesium halogen compound. H. M. D.

Condensation of Acetylenic Nitriles with Alcohols. General Method of Synthesising β -Substituted Derivatives of β -Alkyl-oxyacrylonitriles. CHARLES MOUREU and I. LAZENNEC (*Compt. rend.*, 1906, 142, 338—340. Compare this vol., i, 148).—The acetylenic nitriles, $RC \equiv C \cdot CN$, react energetically with sodium methoxide or ethoxide (1 mol.) in the presence of the corresponding alcohol to form a mixture of the β -alkyloxyethylenic nitrile and β -acetal nitrile in varying proportions: thus, phenylpropionitrile yields β -phenyl- β -methoxyacrylonitrile (β -methoxycinnamitrile), $OMe \cdot CPh \cdot CH \cdot CN$, and the dimethylacetal of cyanoacetophenone [β -dimethoxyphenyl-acetonitrile], $CPh(OMe)_2 \cdot CH_2 \cdot CN$; the mixture boils at 165° under 20 mm. pressure, and it is impossible to separate the constituents by fractional distillation. If, however, alcoholic potassium hydroxide replaces the sodium methoxide or ethoxide in the above reaction, the β -alkyloxyethylenic nitrile is the only product of the reaction, and the following compounds were thus prepared: β -methoxy- β -amylacrylonitrile, $OMe \cdot C(C_5H_{11}) \cdot CH \cdot CN$, boiling at 125 — 131° under 15 mm.

pressure; β -ethoxy- β -amylacrylonitrile, $\text{OEt}\cdot\text{C}(\text{C}_5\text{H}_{11})\cdot\text{CH}\cdot\text{CN}$, boiling at $134\text{--}135^\circ$ under 11 mm. pressure; β -methoxy- β -hexylacrylonitrile, $\text{OMe}\cdot\text{C}(\text{C}_6\text{H}_{13})\cdot\text{CH}\cdot\text{CN}$, boiling at $138\text{--}142^\circ$ under 14 mm. pressure; β -ethoxy- β -hexylacrylonitrile, $\text{OEt}\cdot\text{C}(\text{C}_6\text{H}_{13})\cdot\text{CH}\cdot\text{CN}$, boiling at $141\text{--}143^\circ$ under 14 mm. pressure; β -methoxy- β -phenylacrylonitrile, $\text{OMe}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CN}$, boiling at $159\text{--}166^\circ$ under 14 mm. pressure; β -ethoxy- β -phenylacrylonitrile, $\text{OEt}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CN}$, boiling at $166\text{--}173^\circ$ under 12 mm. pressure, and β -propoxy- β -phenylacrylonitrile, $\text{OPr}^a\cdot\text{CPh}\cdot\text{CH}\cdot\text{CN}$,

boiling at $184\text{--}190^\circ$ under 22 mm. pressure. The alkyloxyacetylenic nitriles derived from phenylpropionitrile are readily hydrolysed by dilute sulphuric acid, forming cyanoacetophenone and an alcohol. The aliphatic derivatives are much more stable; β -ethoxy- β -amylacrylonitrile is only decomposed on prolonged boiling with 50 per cent. sulphuric acid, yielding methyl amyl ketone. M. A. W.

A New Series of Organo-magnesium Compounds containing Ethyl Ether. WLADIMIR TSCHELINZEFF (*Ber.*, 1906, 39, 773—779).—The amount of ethyl ether which will combine with magnesium propyl iodide and with magnesium *i*-amyl iodide was determined by distilling off the excess of ethyl ether remaining after causing weighed quantities of propyl iodide and magnesium to combine in ethereal solution, and weighing the product; the quantity of ethyl ether combined with the magnesium alkyl iodide points to the existence of derivatives of the type $\text{MgRI}, 2\text{Et}_2\text{O}$. That such compounds are formed also appears evident from the fact that, on adding ethyl ether to a solution of propyl or *i*-amyl iodide in benzene containing magnesium, equal quantities of heat are developed for each of the two first mols. of ethyl ether added; the subsequent addition of ether causes little thermal disturbance.

The bearing of these facts on the Grignard syntheses is discussed. Hitherto, the ether derivatives have been assumed to have the composition $\text{RMgI}, \text{Et}_2\text{O}$, based on Blaise's analyses (*Abstr.*, 1901, i, 317). W. A. D.

Influence of Alkyloxy-groups on the Reactivity of α -Halogen Atoms in Aromatic Compounds. GUIDO GOLDSCHMIEDT (*Ber.*, 1906, 39, 651—652. Compare A. Werner, this vol., i, 180).—Attention is drawn to earlier work (*Abstr.*, 1898, i, 31; 1899, i, 140; 1900, i, 35; 1902, i, 40, 41; 1903, i, 64; also Hertzka, *Abstr.*, 1905, i, 291) in which mention has been made of the influence of alkyloxy-groups on the replacement of α -chlorine atoms by methoxy- or ethoxy-groups. J. J. S.

Nitrostilbenes. FRANZ SACHS and SIEGFRIED HILPERT (*Ber.*, 1906, 39, 899—906. Compare Sachs and Kempf, *Abstr.*, 1902, i, 682; Sachs and Hilpert, *Abstr.*, 1904, i, 876).—In continuation of their studies on the action of light on chemical compounds, the authors have examined aromatic compounds where the groups $-\text{NO}_2$ and $\text{CH}\cdot\text{CH}$ are in the ortho-position to one another. In the cases examined, no intramolecular reduction and oxidation were observed, as in the case

of *o*-nitrobenzaldehyde; neither, as with nitrobenzaldoxime, was any stereochemical transformation observed; on the other hand, polymerisation took place.

When 2:4-dinitrostilbene is exposed to light for a month, it undergoes polymerisation to the compound $C_{28}H_{20}O_8N_4$, which crystallises from glacial acetic acid in rhombic plates and melts at 199–200°. Determinations of its molecular weight by the ebullioscopic method in acetone showed that the compound has the formula given.

When 2-nitro-4-aminostilbene is diazotised by Knoevenagel's amyl nitrite method, the *diazo-sulphate*, $C_{14}H_{11}O_6N_3S$, is formed; this crystallises in needles, decomposes at 108°, and explodes at 165°; the *diazo-nitrate*, $C_{14}H_{10}O_5N_4$, crystallises in needles, whilst the *diazo-chloride*, $C_{14}H_{10}O_2N_3Cl$, decomposes at 120°. By the action of sulphuric acid on a boiling solution of 4-diazo-2-nitrostilbene sulphate, 2-nitrostilbene, $C_{14}H_{11}O_2N$, is formed; it separates from alcohol in needles and melts at 76°.

4-Hydrazino-2-nitrostilbene, $C_{14}H_{13}O_2N_3$, prepared by the action of a solution of stannous chloride in hydrochloric acid on a solution of the diazonium sulphate in hydrochloric acid, separates from a mixture of alcohol and light petroleum in red crystals and melts at 125°. The compound $C_{21}H_{15}O_6N_5$, formed by the condensation of 4-hydrazino-2-nitrostilbene with 2:4-dinitrobenzaldehyde in glacial acetic acid solution, forms dark brown needles and decomposes at 280°.

2-Aminostilbene, $C_{14}H_{13}N$, prepared by the reduction of 2-nitrostilbene with stannous chloride in glacial acetic acid solution, crystallises in leaflets and melts at 106°; its ethereal solution exhibits blue fluorescence. Its *acetyl* derivative separates from alcohol in needles and melts at 140°.

2-Diazo-4-nitrostilbene sulphate, $C_{14}H_9O_6N_3S$, decomposes at 135–157°; the corresponding *chloride* decomposes at 107°.

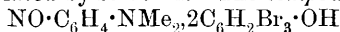
The *azo*-compound, $C_{24}H_{17}O_3N_3$, formed by coupling 4-diazo-2-nitrostilbene with β -naphthol, melts at 220°; when phenol is substituted for β -naphthol, the *azo*-compound, $C_{20}H_{15}O_3N_3$, is formed; the latter crystallises in dark yellow needles and melts at 192°.

When 2-diazo-4-nitrostilbene sulphate is coupled with aniline, it forms 2-benzenediazoamino-4-nitrostilbene, $C_{20}H_{16}O_2N_4$, which separates from acetone in reddish-yellow needles and melts at 146°. It undergoes transformation in the presence of aniline hydrochloride into 5'-nitro-4-amino-2'-styrylazobenzene, $C_{20}H_{16}O_2N_4$, which crystallises from light petroleum in bright red needles and melts at 105°; its *hydrochloride* forms needles with the lustre of cantharides and melts at 212°.

The action of light on 2-nitrostilbene yielded resinous substances, the nature of which has not yet been elucidated. A. McK.

Additive Compounds of *p*-Nitrosodimethylaniline with certain Phenols. HENRY A. TORREY and J. A. GIBSON (*Amer. Chem. J.*, 1906, 35, 246–253).—It has been shown by Torrey and Hardenbergh (*Abstr.*, 1905, i, 218) that quinhydrone and phenonone are dissociated in benzene solution into quinone and quinol, and quinone and phenol, respectively. *p*-Nitrosodimethylaniline forms

additive compounds with certain substituted phenols which dissociate in a similar manner. Ebullioscopic determinations of the molecular weight of the compound $\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2, 2\text{C}_6\text{H}_2\text{Cl}_3 \cdot \text{OH}$, described by Edeleanu and Euescu (Abstr., 1896, i, 359), show that this substance is completely dissociated by solvents. The compound



forms dark red crystals and dissolves in chloroform, alcohol, acetone, benzene, or ether to form green solutions; ebullioscopic determinations show that the compound is completely dissociated when dissolved in benzene. The additive compound of salicylic acid and *p*-nitrosodimethylaniline, $\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2, 2\text{C}_6\text{H}_4(\text{OH}) \cdot \text{CO}_2\text{H}$, crystallises in slender, dark red needles, melts at 110° , and dissolves in benzene to form a green solution. The additive compound,



(Edeleanu and Euescu, *loc. cit.*), obtained by the union of *p*-nitrosodimethylaniline with trichlororesorcinol, forms dark blue crystals, dissolves in benzene, ether, chloroform, alcohol, or acetone to form green solutions, and is completely dissociated in benzene solution. The tribromoresorcinol compound, $2\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2, \text{C}_6\text{HBr}_3(\text{OH})_2$, is obtained in olive-green crystals, melts at 115° , and is soluble in benzene, chloroform, acetone, alcohol, or ether, forming green solutions. The catechol compound, $2\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2, \text{C}_6\text{H}_4(\text{OH})_2$, forms olive-green crystals, melts and decomposes at 125° , and yields green solutions. The constitution of these additive compounds is discussed.

Attempts to prepare similar compounds with pyrogallol and tetrachlorocatechol were unsuccessful. E. G.

Sulphonation of Thioaniline. OTTO SCHMIDT (*Ber.*, 1906, 39, 611—616. Compare Merz and Weith, this Journal, 1871, 24, 566; Nietzki and Bothof, Abstr., 1895, i, 132; Armstrong and Berry, Proc., 1900, 16, 159).—4 : 4'-Diaminodiphenylsulphide-2 : 2'-disulphonic acid, $\text{S}[\text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{SO}_3\text{H}]_2$, is prepared (1) by dissolving finely-powdered thioaniline in warm concentrated sulphuric acid and treating the cooled solution with sulphuric acid containing 60 per cent. of sulphur trioxide, or (2) by boiling sodium and chloro-4-nitrobenzene-2-sulphonate with sodium sulphide in aqueous solution and reducing the product with zinc dust and hydrochloric acid. It forms a white powder, is insoluble in water, and when diazotised in dilute hydrochloric acid solution under cooling with ice forms the bisdiazonium anhydride, $\text{S}(\text{C}_6\text{H}_4 \text{---} \text{N}_2 \text{---} \text{SO}_2 \text{---} \text{O})_2$, which, on dilution of its solution in concentrated nitric acid, separates in small, bronze leaflets, detonates at $120 - 123^\circ$, is very sensitive to light, and is insoluble in the usual solvents. It remains unchanged when boiled with water or methyl or ethyl alcohol, and is not decomposed completely when boiled with dilute sulphuric acid for three-quarters of an hour. When treated with sulphur dioxide and copper powder in dilute sulphuric acid solution, made alkaline, evaporated to dryness, and fused with potassium hydroxide, the bisdiazonium anhydride yields thiocatechol, 2 : 2'-dihydroxydiphenyl disulphide, and catechol. G. Y.

Derivatives of Palladosammine. ALEXANDER GUTBIER and A. KRELL (*Ber.*, 1906, 39, 616—621. Compare this vol., i, 12; Gutbier, *Abstr.*, 1905, i, 584, 876).—Double salts of palladous chloride or bromide, with the hydrochlorides or hydrobromides of benzylamine and dibenzylamine, are formed by mixing the components in hydrochloric acid solution or by adding the base in small quantities to a dilute solution of the palladous salt and recrystallising the precipitate from alcohol.

Benzylamine palladous chloride, $\text{Pd}[\text{NH}_3(\text{CH}_2\text{Ph})\text{Cl}]_2\text{Cl}_2$, separates from hydrochloric acid in needles or leaflets or from alcohol in glistening, golden-brown leaflets. The *bromide*, $\text{Pd}[\text{NH}_3(\text{CH}_2\text{Ph})\text{Br}]_2\text{Br}_2$, forms dark red needles or leaflets. *Dibenzylamine palladous chloride*, $\text{Pd}[\text{NH}_2(\text{CH}_2\text{Ph})_2\text{Cl}]_2\text{Cl}_2$, crystallises in short, brown needles or from alcohol in dark yellowish-red leaflets or long, brown needles. The *bromide*, $\text{Pd}[\text{NH}_2(\text{CH}_2\text{Ph})_2\text{Br}]_2\text{Br}_2$, separates from hydrochloric acid in glistening, reddish-brown needles or from alcohol in leaflets.

Dibenzylpalladosammine chloride, $\text{Pd}(\text{NH}_2\cdot\text{CH}_2\text{Ph})_2\text{Cl}_2$, is formed by the action of an excess of benzylamine on a neutral, aqueous solution of a palladochloride and addition of concentrated hydrochloric acid to the product. It crystallises in yellow leaflets, and when dissolved in ammonia and treated with concentrated hydrochloric acid yields palladosammine chloride. The *bromide*, $\text{Pd}(\text{NH}_2\cdot\text{CH}_2\text{Ph})_2\text{Br}_2$, forms small, yellow leaflets, and on treatment with ammonia and concentrated hydrobromic acid yields palladosammine bromide. *Tetra-benzylpalladosammine chloride*, $\text{Pd}[\text{NH}(\text{CH}_2\text{Ph})_2]_2\text{Cl}_2$, crystallises from alcohol in glistening, golden leaflets and is converted into palladosammine chloride by ammonia. The *bromide*, $\text{Pd}[\text{NH}(\text{CH}_2\text{Ph})_2]_2\text{Br}_2$, forms golden leaflets, and when treated with concentrated hydrobromic acid in hot ammoniacal solution yields palladosammine bromide.

Palladodipyridine chloride (Rosenheim and Maass, *Abstr.*, 1899, i, 163) is formed by the action of pyridine on a palladous chloride or a chloropalladite solution; when heated with ammonia, it evolves pyridine and forms palladosammine chloride. The *bromide*, $\text{Pd}(\text{C}_5\text{NH}_5)_2\text{Br}_2$, forms a yellow, microcrystalline precipitate and yields palladosammine bromide when heated with ammonia.

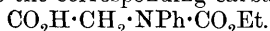
Palladodi-2-methylpyridine chloride, $\text{Pd}(\text{C}_5\text{NH}_4\text{Me})_2\text{Cl}_2$, crystallises from alcohol in yellow leaflets, dissolves in an excess of 2-methylpyridine, from its solution in which it is reprecipitated unchanged on addition of concentrated hydrochloric acid, and on treatment with ammonia and hydrochloric acid yields palladosammine chloride. The *bromide*, $\text{Pd}(\text{C}_5\text{NH}_4\text{Me})_2\text{Br}_2$, crystallises in yellowish-red leaflets and is converted into palladosammine bromide by treatment with ammonia.

Palladodiquinoline chloride, $\text{Pd}(\text{C}_9\text{NH}_7)_2\text{Cl}_2$, is obtained as a yellow precipitate, which is readily soluble in ammonia. The *bromide*, $\text{Pd}(\text{C}_9\text{NH}_7)_2\text{Br}_2$, crystallises in reddish-brown, microscopic leaflets. When dissolved in hot aqueous ammonia and treated with concentrated hydrochloric or hydrobromic acid, the palladodiquinoline salts are converted into palladosammine chloride or bromide respectively.

G. Y.

Action of Ethyl Chlorocarbonate on Aromatic Glycines.

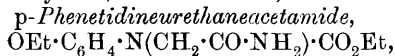
AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and HENRI BARBIER (*Bull. Soc. chim.*, 1906, [iii], 35, 123—126).—Phenylglycine reacts with ethyl chlorocarbonate to give the corresponding carbamate,



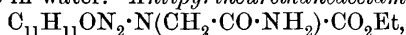
This is a colourless, viscous liquid, which decomposes when heated and is very soluble in alcohol and ether. The *sodium* and *silver* salts are crystalline; the former melts at 231°. The *amide*, prepared by treating phenylglycineamide with ethyl chlorocarbonate, crystallises from alcohol and melts at 124°, and on prolonged boiling with a dilute solution of sodium hydroxide is transformed partly into phenylglycine and partly into phenylhydantoin. The *ethyl* ester, obtained by treating phenylglycine ester with ethyl chlorocarbonate, is a viscous liquid with a slight pleasant odour, boils at 187—188° under 14 mm. pressure, and decomposes above 300° when heated under atmospheric pressure.

Similar derivatives are obtainable from aromatic glycineamides by the action of ethyl chlorocarbonate. The following substances were prepared in this way.

p-Tolylurethaneacetamide, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}(\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2)\cdot\text{CO}_2\text{Et}$, forms slender, colourless crystals, melts at 153°, and is slightly soluble in alcohol or ether.



forms slender, colourless needles, melts at 140°, and is easily soluble in alcohol, insoluble in water.

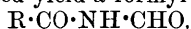


forms colourless needles, melts at 181°, and is soluble in alcohol or water.

T. A. H.

N-Methylol Compounds of the Acid Amides. ALFRED EINHORN (*Annalen*, 1905, 343, 207—310).—Nitrogen methylol compounds have been obtained by the interaction of acid imides and formaldehyde, but the corresponding reaction has not hitherto been carried out with acid amides. The condensation takes place most readily in an alkaline medium, for example, in the presence of alkali hydroxides, carbonates or cyanides, and organic bases; in many cases, acids will act as condensing agents. An intermediary glycol seems to be formed in the reaction, thus: $\text{R}\cdot\text{CO}\cdot\text{NH}_2 + \text{OH}\cdot\text{CH}_2\cdot\text{OH} = \text{H}_2\text{O} + \text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$.

The compounds produced are true condensation and not additive products, and when oxidised yield a formyl derivative,



These compounds do not yield salts, but are hydrolysed by acids, formaldehyde being produced. Sodium hydrogen sulphite and ammonia behave in a similar manner. They do not yield acyl derivatives, but with acetic anhydride lose water and formaldehyde, methylenedibenzamide being produced; with benzoyl chloride in an alkaline medium, water is eliminated and the methylol compound of methylenedibenzamide formed; the latter readily decomposes into formaldehyde and methylenedibenzamide.

The methylol compounds occasionally interact with acid amides, forming diacylated methylenediamines.

Most monocyclic and aromatic compounds condense with this class of

substances very easily, especially hydrocarbons, phenolcarboxylic acids, hydroxy-acids, sulphonic acids, and acylated bases. Generally 1 molecule of the methylol compound replaces one hydrogen of the cyclic nucleus, but occasionally two hydrogens are replaced, diamines being formed.

Methylol compounds of *N*-alkylated acid amides cannot be prepared.

[With EDUARD BISCHKOPFF and BRUNO SZELINSKI.] —*N*-Methylolbenzamide, $\text{COPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$, prepared by adding a 40 per cent. solution of formaldehyde to a suspension of benzamide in a 3 per cent. solution of potassium carbonate, crystallises in six-sided plates melting at $104\text{--}106^\circ$; with ammonia, it yields hexamethylenetriamine. *N*-Methylenedibenzamide, $\text{COPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NBz}\cdot\text{CH}_2\cdot\text{OH}$, prepared from the compound last mentioned by the Schotten-Baumann method or by the action of formaldehyde in the presence of dilute sulphuric acid, forms crystals sintering and then melting at $182\cdot5^\circ$; it readily loses formaldehyde, yielding methylenedibenzamide, which can also be prepared from benzamide and formaldehyde in the presence of dilute acids, and crystallises in needles melting at $218\text{--}219^\circ$. Methylenedibenzamide-carboxylic acid, $\text{CH}(\text{NHBz})_2\cdot\text{CO}_2\text{H}$, prepared from benzamide and glyoxylic acid, crystallises in needles melting and decomposing at 234° . Formylbenzamide (benzoylaminoformaldehyde), $\text{NHBz}\cdot\text{CHO}$, prepared by oxidising methylolbenzamide by potassium dichromate and sulphuric acid, crystallises in prismatic needles melting at 120° , and from benzene with C_6H_6 in needles melting at 84° ; it yields neither a semicarbazone nor a phenylhydrazone; with semicarbazide, the formyl group is eliminated, and with phenylhydrazine *s*-formylphenylhydrazine (m. p. 146°) is produced. 2:5-Diphenyl-1:2:4-triazole, $\text{C}_{14}\text{H}_{11}\text{N}_3$, crystallises in colourless needles melting at $96\text{--}97^\circ$, and is volatile without decomposition; the hydrochloride crystallises in needles melting and decomposing at 180° , and the platinichloride in dark yellow plates decomposing at 218° ; the picrate crystallises in rhombic plates melting at 148° .

N-Diethylaminemethylbenzamide (benzoyldiethylmethylenediamine), $\text{COPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NEt}_2$, prepared by heating together methylolbenzamide and diethylamine, crystallises in colourless plates melting at $62\text{--}64^\circ$; the platinichloride forms needles melting at 158° , and the picrate yellow needles melting at 125° .

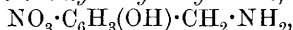
N-Piperidylmethylbenzamide, $\text{COPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_{10}$, prepared from the methylolbenzamide and piperidine, or from benzamide, piperidine, and formaldehyde solution, crystallises in prisms melting at $128\text{--}129^\circ$.

N-Benzoylhydroxymethylisopropylbenzylamine,

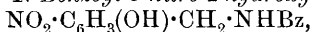
$\text{OH}\cdot\text{C}_6\text{H}_2\text{MePr}^i\cdot\text{CH}_2\cdot\text{NHBz}$ [$\text{Me}:\text{Pr}:\text{OH}:\text{CH}_2=1:4:3:?$], prepared from thymol and methylolbenzamide in the presence of hydrochloric acid, crystallises in needles melting at $168\text{--}169^\circ$. *N*-Benzoyl-*o*-dihydroxybenzylamine, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}_2\cdot\text{NHBz}$, prepared from methylolbenzamide and *o*-dihydroxybenzene, crystallises in needles melting and decomposing at 270° . *N*-Benzoyl-*o*-hydroxymethoxybenzylamine, $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}_2\cdot\text{NHBz}$, prepared from guaiacol and methylolbenzamide, crystallises in rhombic plates melting at 148° and forms a sparingly soluble sodium salt; its

acetyl derivative crystallises in rhombic plates melting at 161° . *N-Benzoyl-2:5-dihydroxybenzylamine*, prepared from quinol and methylolbenzamide, crystallises in white crystals melting and decomposing at 270° . *N-Dibenzoyl-1:2:3-trihydroxyxylylenediamine*, $\text{C}_6\text{H}(\text{OH})_3(\text{CH}_2\cdot\text{NHBz})_2$, prepared from pyrogallol and methylolbenzamide, crystallises in colourless prisms or needles melting at 199° .

N-Benzoyl-3-nitro-4-hydroxybenzylamine, $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}_2\cdot\text{NHBz}$, prepared from *o*-nitrophenol and methylolbenzamide in the presence of sulphuric acid at a low temperature, crystallises in yellow needles melting at 137° . The corresponding *amino*-derivative is obtained by reduction of the nitro-compound with tin and hydrochloric acid, and crystallises in colourless, microscopic needles melting and decomposing at 215° . *3-Nitro-4-hydroxybenzylamine*,



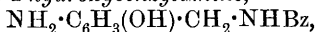
prepared by hydrolysis of the benzoyl derivative with hydrochloric acid, crystallises in dark orange-red needles, which at 115° lose water, becoming light yellow, and melt at 225° . *3-Amino-4-hydroxybenzylamine dihydrochloride*, prepared by reducing the compound last mentioned, forms grey crystals. *N-Benzoyl-5-nitro-2-hydroxybenzylamine*,



prepared from *p*-nitrophenol and methylolbenzamide in the presence of sulphuric acid, crystallises in yellow needles melting at $217\text{--}218^{\circ}$. On hydrolysis with alcoholic potash, it yields the corresponding *base*, which crystallises in golden-yellow leaflets melting and decomposing at 250° ; when treated with nitrous acid, it yields the corresponding benzyl alcohol (m. p. 126°); the *hydrochloride* of the base crystallises in yellow needles melting and decomposing at 250° .

3-Nitro-2-hydroxybenzyl chloride does not yield benzylamine when treated either with ammonia or potassium phthalimide, but it reacts with diethylamine and ethylaniline. *5-Nitro-2-hydroxybenzyl diethylamine*, $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}_2\cdot\text{NEt}_2$, crystallises in pale yellow needles melting at $68\text{--}69^{\circ}$; its *hydrochloride* forms colourless crystals melting and decomposing at 197° . *Phenyl-5-nitro-2-hydroxybenzylethylamine*, $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}_2\cdot\text{NEtPh}$, forms yellow prisms sintering and then melting at 126° . When reduced, it forms the corresponding *amino*-compound.

N-Benzoyl-5-amino-2-hydroxybenzylamine,

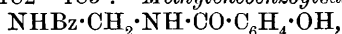


prepared by reducing the corresponding nitro-compound, crystallises in colourless needles melting at 186° . Its *hydrochloride* melts and decomposes at 157° ; when hydrolysed, it yields the *dihydrochloride*, $\text{HCl}\cdot\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{HCl}$, crystallising in white needles melting above 300° .

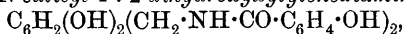
N-Benzoyl- β -hydroxynaphthylmethylamine, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\cdot\text{NHBz}$, prepared from β -naphthol and methylolbenzamide, crystallises in colourless prisms melting at 186° . *N-Benzoyl-2-hydroxyquinolylmethylamine*, $\text{OH}\cdot\text{C}_9\text{H}_5\cdot\text{CH}_2\cdot\text{NHBz}$, from 2-hydroxyquinoline and methylolbenzamide, forms crystals melting at 186° ; its *hydrochloride* crystallises in lemon-yellow prisms melting and decomposing at 151° . *N-Benzoylbenzylaminecarboxylic* [*ω -benzoylamino-m-toluic*] acid, $\text{NHBz}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, forms crystals melting at 186° .

[With GUSTAV SCHUPP.]—*N-Methylolsalicylamide*,
 $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$,

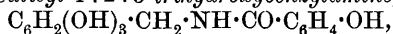
prepared from salicylamide and formaldehyde in an alkaline medium, crystallises in prismatic needles melting at 126—128°; if excess of formaldehyde is used, and potassium cyanide be used as condensing agent, the compound $\text{C}_{15}\text{H}_{16}\text{O}_5\text{N}_2$, crystallising in prismatic needles melting at 114—116°, is obtained. It is soluble in alkali hydroxides and gives a violet coloration with ferric chloride. *Methylenedisalicylamide*, $\text{CH}_2(\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2$, prepared from methylolsalicylamide and salicylamide, crystallises in needles melting at 195—197° and is soluble in alkali hydroxides. *Dibenzoylmethylenesalicylamide*, $\text{CH}_2(\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OBz})_2$, prepared from methylenedisalicylamide and benzoyl chloride in the presence of pyridine, crystallises in prismatic needles melting at 182—183°. *Methylenebenzoylsalicylamide*,



prepared from methylolsalicylamide and benzamide, crystallises in prismatic needles sintering and then melting at 151—153°. *N-Piperidylmethylsalicylamide*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_{10}$, prepared from salicylamide, piperidine, and formaldehyde, crystallises in microscopic needles melting at 93—95°. When methylolsalicylamide is benzoylated in pyridine, *dibenzoylsalicyliminodimethyl ether*, $(\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NBz}\cdot\text{CH}_2)_2\text{O}$, is obtained, crystallising in prismatic needles melting at 184—185°. *N-Salicylhydroxymethylisopropylbenzylamine*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{MePr}^s\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, prepared from methylolsalicylamide and thymol, crystallises in needles melting at 170—172°. *Di-N-salicyl-1:2-dihydroxyxylylenediamine*,



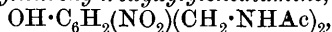
prepared from methylolsalicylamide and *o*-dihydroxybenzene, is a crystalline powder melting at 200—203° and soluble in, but decomposed by, alkali hydroxides. *Di-N-salicyl-1:4-dihydroxyxylylenediamine*, prepared from quinol, is a crystalline powder decomposing at 250—252°. *N-Salicyl-1:2:3-trihydroxybenzylamine*,



prepared from pyrogallol and methylolsalicylamide, crystallises in needles melting and decomposing at 195—197°.

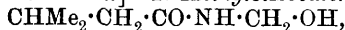
[With CARL LADISCH.]—*Methylolformamide*, $\text{HCO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$, prepared from formaldehyde and formamide in an alkaline medium, is a colourless oil. When condensed with *p*-nitrophenol, *N-formylnitrohydroxybenzylamine*, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CHO}$, is obtained as yellow, prismatic needles melting and decomposing at 236°.

Methylolacetamide, $\text{NHAc}\cdot\text{CH}_2\cdot\text{OH}$, prepared from acetamide and formaldehyde in an alkaline medium, forms crystals melting at 50—52°. *N-Diacetylnitrohydroxyxylylenediamine*,



prepared from methylolacetamide and *p*-nitrophenol in the presence of concentrated sulphuric acid, crystallises in yellow prisms or leaflets melting at 196°.

[With EDUARD SPRÖNGERTS.]—*N-Methylolisovaleramide*,

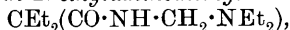


prepared from isovaleramide and formaldehyde in the presence of potassium carbonate, crystallises in needles melting at 76—79°.

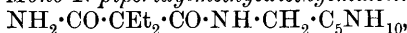
Methylenediisovaleramide, $\text{CH}_2(\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHMe}_2)_2$, prepared by heating methylolisovaleramide at 90° , or from isovaleramide and methylolisovaleramide, crystallises in needles melting at 191° . *N-Diethylaminomethylisovaleramide*, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NEt}_2$, prepared from diethylamine, isovaleramide, and formaldehyde, is a pale yellow oil; the *picrate* crystallises in yellow needles melting at 132° . *N-Piperidylmethylisovaleramide*, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_{10}$, prepared from isovaleramide, piperidine, and formaldehyde, is a pale yellow, thick oil yielding a *picrate* melting at 183° .

N-Methyloldiethylacetamide, $\text{CHEt}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$, prepared from diethylacetamide and formaldehyde in the presence of alkali, crystallises in prisms melting at $87-88^\circ$. *N-Diethylaminomethyldiethylacetamide*, $\text{CHEt}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NEt}_2$, prepared from diethylacetamide, diethylamine, and formaldehyde, is a semi-solid mass; the *acid tartrate* crystallises with $2\text{H}_2\text{O}$ and melts at 67° . *N-Piperidylmethyldiethylacetamide*, $\text{CHEt}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_{10}$, prepared from diethylacetamide, piperidine, and formaldehyde, crystallises in needles melting at 125° ; its *hydrochloride* melts at 121° and its *hydrobromide* at 145° .

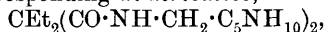
s-N-Dimethyloldiethylmalonamide, $\text{CEt}_2(\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH})_2$, prepared from diethylmalonamide and formaldehyde in the presence of barium hydroxide, crystallises in leaflets melting at 141° . *s-N-Diformyldiethylmalonamide*, $\text{CEt}_2(\text{CO}\cdot\text{NH}\cdot\text{CHO})_2$, prepared from the compound last mentioned by oxidation with chromic acid mixture, forms granular crystals melting at 178° . *Mono-N-diethylaminomethyldiethylmalonamide*, $\text{NH}_2\cdot\text{CO}\cdot\text{CEt}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NEt}_2$, prepared from diethylmalonamide, diethylamine, and formaldehyde, forms crystals melting at 109° ; at the same time, the *di-N-ethylaminomethyldiethylmalonamide*,



is formed and is separated from the mono-derivative by taking advantage of its solubility in petroleum; it crystallises in needles melting at 86° . *Mono-N-piperidylmethyldiethylmalonamide*,



prepared from diethylmalonamide, piperidine, and formaldehyde, crystallises in needles melting at $136-141^\circ$ and is insoluble in carbon disulphide; the corresponding *di-derivative*,



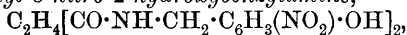
which is formed at the same time as the compound last mentioned, crystallises in plates melting at $115-119^\circ$ and is soluble in carbon disulphide.

[With CARL LADISCH.]—*N-Dimethylolsuccinamide*,



prepared from succinamide and formaldehyde in the presence of aqueous potassium carbonate, forms crystals melting and decomposing at 167° .

Succinylxyllylenediamine, $\text{C}_6\text{H}_4\begin{matrix} \text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2 \end{matrix}$, prepared from dimethylolsuccinamide and benzene in presence of concentrated sulphuric acid, forms a yellow, amorphous solid melting and decomposing at about 225° . *N-Succinyl-5-nitro-2-hydroxybenzylamine*,

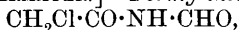


prepared from *p*-nitrophenol and methylolsuccinamide in the presence of concentrated sulphuric acid, forms white crystals melting at 257°

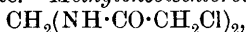
and is decomposed by heating with hydrochloric acid into succinic acid and *m*-nitro-*o*-hydroxybenzylamine. *N*-Succinyl- β -hydroxynaphthylmethylamine, $C_2H_4(CO \cdot NH \cdot CH_2 \cdot C_{10}H_6 \cdot OH)_2$, prepared from β -naphthol and dimethylolsuccinamide in the presence of dilute alcoholic hydrochloric acid, crystallises in needles melting at 222—224°.

N-Methylolchloroacetamide, $CH_2Cl \cdot CO \cdot NH \cdot CH_2 \cdot OH$, prepared from monochloroacetamide and formaldehyde in the presence of hydrochloric acid, crystallises in colourless prisms melting at 91—102°. *N*-Methyloltrichloroacetamide, $CCl_3 \cdot CO \cdot NH \cdot CH_2 \cdot OH$, prepared from trichloroacetamide and formaldehyde in the presence of dilute sulphuric acid, crystallises in needles melting at 99—100°. *N*-Methylolbromoacetamide, prepared from bromoacetamide and formaldehyde in the presence of hydrochloric acid, forms crystals melting at 94—95°. *N*-Methylol- α -bromopropionamide, $CH_3 \cdot CHBr \cdot CO \cdot NH \cdot CH_2 \cdot OH$, prepared from α -bromopropionamide and formaldehyde, crystallises in prismatic needles melting at 93—95° and decomposes when heated with the elimination of formaldehyde. *N*-Methyloliodoacetamide, prepared from iodoacetamide and formaldehyde, crystallises in leaflets melting at about 130°.

[With THEODOR MAUERMAYER.]—*Formylchloroacetamide*,



prepared by oxidising *N*-methylchloroacetamide, forms crystals melting at 89—90°, yields no hydrogen sulphite compound, but reduces ammoniacal silver nitrate. *Methylenebischloroacetamide*,

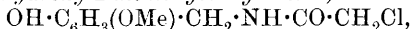


prepared from methylolchloroacetamide and concentrated sulphuric acid, crystallises in leaflets melting at 175°. *N*-Chloroacetylhydroxymethylisopropylbenzylamine, $OH \cdot C_6H_2MePr^B \cdot CH_2 \cdot NH \cdot CO \cdot CH_2Cl$, prepared from thymol and methylolchloroacetamide, crystallises in needles melting at 152—153°. *N*-Chloroacetyl-3-nitro-4-hydroxybenzylamine, $OH \cdot C_6H_3(NO_2) \cdot CH_2 \cdot NH \cdot CO \cdot CH_2Cl$, prepared from *o*-nitrophenol and methylolchloroacetamide in the presence of sulphuric acid, crystallises in pale yellow needles melting at 106—107°. The corresponding 5-nitro-2-hydroxy-compound is prepared in a similar manner, using *p*-nitrophenol, and crystallises in needles melting at 185—186°, and when heated with diethylamine is converted into *N*-diethylglycyl-5-nitro-2-hydroxybenzylamine hydrochloride,

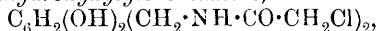


which crystallises in needles melting at 199°; the free base crystallises in yellow needles melting at 150°. *N*-Bischloroacetyl-1-nitro-4-ethoxyxylylenediamine, $NO_2 \cdot C_6H_2(OEt) \cdot (CH_2 \cdot NH \cdot CO \cdot CH_2Cl)_2$, prepared from *p*-nitrophenetole and methylolchloroacetamide in the presence of sulphuric acid, crystallises in needles melting at 184°. 1-Nitro-4-ethoxyxylylenediamine hydrochloride, $NO_2 \cdot C_6H_2(OEt)(CH_2 \cdot NH_2, HCl)_2$, prepared by boiling the compound last mentioned with hydrochloric acid, crystallises in needles which carbonise without melting and yields on oxidation with permanganate a compound melting at 176°, probably 1-nitro-4-phenetole dicarboxylic acid. Bisdiethylglycyl-1-nitro-4-ethoxyxylylenediamine, $NO_2 \cdot C_6H_2(OEt)(CH_2 \cdot NH \cdot CO \cdot CH_2 \cdot NEt_2)_2$, prepared from bischloroacetylnitroethoxyxylylenediamine and diethylamine, crystallises in needles melting at 118—119°. *N*-Chloroacetyl-1:2-dihydroxybenzyl-

amine, $C_6H_3(OH)_2 \cdot CH_2 \cdot NH \cdot CO \cdot CH_2Cl$, prepared from *o*-dihydroxybenzene and methylolchloroacetamide, crystallises in colourless prisms melting at $140-141^\circ$. 1:2-Dihydroxybenzylamine hydrochloride, $C_6H_3(OH)_2 \cdot CH_2 \cdot NH_2 \cdot HCl$, prepared by boiling chloroacetyldihydroxybenzylamine with dilute hydrochloric acid, crystallises in needles melting at 169° . The borate of *N*-diethylglycyl-1:2-dihydroxybenzylamine, $C_6H_3(OH)_2 \cdot CH_2 \cdot NH \cdot CO \cdot CH_2 \cdot NEt_2 \cdot HBO_2$, is formed when the product of the interaction of chloroacetyldihydroxybenzylamine and diethylamine is treated with an alcoholic solution of boric acid, and is a white, amorphous powder decomposing without melting. *N*-Chloroacetyl-1-hydroxy-2-methoxybenzylamine,



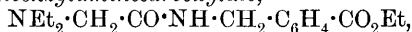
prepared from guaiacol and methylolchloroacetamide in the presence of sulphuric acid, crystallises in needles melting at $116-119^\circ$. *N*-Bischloroacetyl-1:4-dihydroxyxylylenediamine,



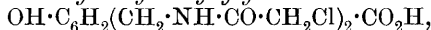
prepared from quinol and methylolchloroacetamide, crystallises in brown needles melting at 235° . *N*-Bischloroacetyl-1:2:3-trihydroxyxylylenediamine, $C_6H(OH)_3(CH_2 \cdot NH \cdot CO \cdot CH_2Cl)_2$, prepared from pyrogallol and methylolchloroacetamide, crystallises in needles melting at $190-191^\circ$. *m*-Chloroacetylbenzylaminocarboxylic [ω -chloroacetyl-amino-*m*-toluic] acid, $CH_2Cl \cdot CO \cdot NH \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$, prepared from methylolchloroacetamide and benzoic acid, crystallises in needles melting at 176° , and when boiled with hydrochloric acid yields *m*-benzylaminocarboxylic acid. Ethyl *m*-chloroacetylbenzylaminocarboxylate, $CH_2Cl \cdot CO \cdot NH \cdot CH_2 \cdot C_6H_4 \cdot CO_2Et$, prepared from the acid last mentioned, crystallises in needles melting at $86-87^\circ$. Ethyl *m*-*N*-piperidylglycylbenzylaminocarboxylate,



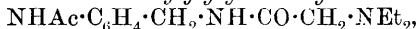
prepared by treating the ester with piperidine, is a thick oil, the hydrochloride of which crystallises in prisms melting at $135-136^\circ$; the hydriodide crystallises in needles melting at 128° , and the periodide crystallises in reddish-brown needles melting at 171° . Ethyl *m*-*N*-diethylglycylbenzylaminocarboxylate,



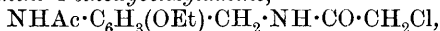
prepared from diethylamine and ethyl chloroacetylbenzylaminocarboxylate, is an oil; its picrate crystallises in golden-yellow leaflets melting at 146° . *N*-Dichloroacetyl-*o*-hydroxyxylylenediaminecarboxylic acid,



prepared from salicylic acid and methylolchloroacetamide, crystallises in needles melting at $196-197^\circ$. *N*-Chloroacetyl-4-acetylaminobenzylamine, $NHAc \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot CO \cdot CH_2Cl$, prepared by condensing methylolchloroacetamide and acetanilide by the aid of sulphuric acid, crystallises in needles melting at $206-207^\circ$ and is hydrolysed to *p*-aminobenzylamine. *N*-Diethylglycyl-4-acetylaminobenzylamine,

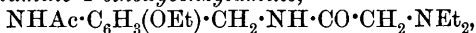


prepared by the action of diethylamine on the compound last mentioned, crystallises in leaflets melting at $116-117^\circ$. *N*-Chloroacetyl-4-acetyl-amino-1-ethoxybenzylamine,

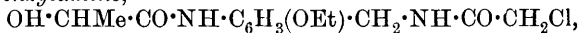


prepared from acetylphenetidine and methylolchloroacetamide, crystal-

lises in needles melting at 179° and is hydrolysed to 4-amino-1-ethoxybenzylamine dihydrochloride, which crystallises in needles melting and decomposing at 276° . The free base is an oil boiling at 300° (not undecomposed), and absorbs carbon dioxide from the air. N-Diethylglycyl-4-acetylamino-1-ethoxybenzylamine,



prepared by the action of diethylamine on the corresponding chloroacetyl derivative, crystallises in leaflets melting at 122° ; the hydrochloride forms hygroscopic leaflets. N-Chloroacetyl-4-lactylamino-1-ethoxybenzylamine,

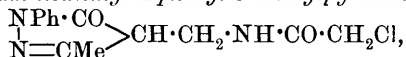


prepared from methylolchloroacetamide and lactyl-*p*-phenetidine, crystallises in needles melting at 116° . N-Diethylglycyl-4-lactylamino-1-ethoxybenzylamine,



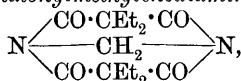
prepared from the compound last mentioned and diethylamine, crystallises in scales melting at 131 – 132° .

4-Chloroacetylaminomethyl-1-phenyl-3-methylpyrazolone,



prepared from methylolchloroacetamide and 1-phenyl-3-methylpyrazolone, crystallises in colourless needles melting at 187° .

N-Methyloltrichloroacetamide and concentrated sulphuric acid yield methylenebistrichloroacetamide, $\text{CH}_2(\text{NH} \cdot \text{CO} \cdot \text{CCl}_3)_2$, which crystallises in colourless leaflets melting at 197° . When treated at a low temperature with 50 per cent. potassium hydroxide, it is converted into methylenediamine, $\text{CH}_2(\text{NH}_2)_2$, which, however, could not be isolated, as it readily decomposes into formaldehyde and ammonia; it was obtained as a dibenzoyl derivative melting at 220° . With diethylmalonic chloride it does not give the expected diethylmalonylmethylenediamine, but bisdiethylmalonylmethylenediamine,



and methylenebisdiethylmalonic acid, $\text{CH}_2(\text{NH} \cdot \text{CO} \cdot \text{CEt}_2 \cdot \text{CO}_2\text{H})_2$. The first compound crystallises in quadratic leaflets melting at 138° ; the second, which is precipitated from the solution of the first by hydrochloric acid, crystallises in scales melting at 189 – 190° , and when heated above its melting point is converted into bisdiethylacetyl-methylenediamine, $\text{CH}_2(\text{NH} \cdot \text{CO} \cdot \text{CHEt}_2)_2$, with the elimination of carbon dioxide.

K. J. P. O.

Benzoylphenylcarbamide. ERNST MOHR (*J. pr. Chem.*, 1906, [ii], 73, 207. Compare Abstr., 1905, i, 890).—Attention is drawn to Stieglitz and Earle's explanation of the formation of benzoylphenylcarbamide from benzoylchloroamide (Abstr., 1904, i, 39, 40).

G. Y.

Hofmann's Reaction. II. ERNST MOHR (*J. pr. Chem.*, 1906, [ii], 73, 177–191. Compare Abstr., 1905, i, 274, 890; Dam and Aberson, Abstr., 1901, ii, 88).—When shaken with 0.3*N* aqueous baryta at

10°, phenylcarbimide dissolves completely in a few minutes, and the solution, which does not give a coloration with bleaching powder, deposits barium phenylcarbamate. This is obtained in a yield of 65—75 per cent. of the theoretical if 1.1 equivalents of baryta are employed, 2 vols. of alcohol added, and the mixture cooled with ice. The product is slightly red and contains traces of carbanilide.

Barium phenylcarbamate, $(\text{NHPh}\cdot\text{CO}_2)_2\text{Ba}\cdot 2\text{H}_2\text{O}$, has, when freshly prepared, an odour of aniline, which disappears when the substance is dried over sulphuric acid in a vacuum; when heated at 100—110°, the salt decomposes, leaving a residue of barium carbonate. In aqueous or slightly alkaline solution at the laboratory temperature, the phenylcarbamate decomposes slowly, forming aniline, carbon dioxide, and barium carbonate; thus, decomposition takes place immediately if the phenylcarbamate is dissolved in warm water, but is hindered by the presence of an excess of baryta. On addition of hydrochloric or acetic acid or carbon dioxide to its aqueous solution, the phenylcarbamate decomposes immediately, forming aniline and carbon dioxide. No odour of phenylcarbimide could be observed.

The action of methyl iodide and methyl alcohol on barium phenylcarbamate leads to the formation of aniline, dimethylaniline and its methiodide, and probably of methylaniline.

Phenylcarbimide is decomposed only extremely slowly when shaken with 0.98*N* hydrochloric acid at 0°. G. Y.

Synthesis of Three Secondary Dimethylcyclohexanols. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1906, 142, 553—555. Compare Abstr., 1904, i, 156; 1905, i, 275).—When 1:2:4-xylenol is directly hydrogenated in the presence of reduced nickel at 190—200°, two-thirds of the phenol is reduced to *o*-xylene, the remaining one-third to a mixture of three parts of the corresponding dimethylcyclohexanol and one of the dimethylcyclohexanone. 1:2-Dimethyl-4-cyclohexanol is a colourless liquid with an odour similar to that of cyclohexanol; it boils at 189° (corr.), has a sp. gr. 0.9261 at 0°/4° or 0.9073 at 16°/4°, n_D 1.458 at 16°, forms a phenylcarbamate crystallising in needles or rhombic plates which melt at 119°, and when oxidised by chromic acid or heated with copper at 300° yields 1:2-dimethyl-4-cyclohexanone, a colourless liquid with an agreeable odour, which boils at 187° (corr.) and forms a crystalline derivative with sodium hydrogen sulphite and a crystalline semicarbazone melting and decomposing at 175°.

1:3-Dimethyl-4-cyclohexanol is the chief product obtained by the direct hydrogenation of 1:3:4-xylenol in the presence of reduced nickel at 190—200°; it is a colourless liquid which boils at 176.5° (corr.), has a sp. gr. 0.9235 at 0°/4° or 0.9119 at 16°/4°, and n_D 1.458 at 16°; the phenylcarbamate forms brilliant prisms melting at 96°; the acetate is a colourless liquid with a penetrating and agreeable odour, which boils at 198° (corr.), has a sp. gr. 0.9405 at 14°/0°, and n_D 1.442 at 14°; the corresponding dimethylcyclohexene (compare Abstr., 1905, i, 588) is obtained by the action of zinc chloride on the alcohol; it has a sp. gr. 0.8122 at 12°/4° and n_D 1.451 at 12°; and the corresponding 1:3-dimethyl-4-cyclohexanone is a colourless liquid which boils at

176.5° (corr.), has a sp. gr. 0.9210 at 0°/4° or 0.9124 at 16°/4°, n_D 1.446 at 16°, and forms a crystalline derivative with sodium hydrogen sulphite and a *semicarbazone* which melts at 190°.

1:4-Dimethyl-2-cyclohexanol is obtained by the direct hydrogenation of 1:4:2-xylol and the yield is 90 per cent.; it is a colourless liquid with an agreeable odour, which boils at 178.5° (corr.), has a sp. gr. 0.9218 at 0°/4° or 0.9037 at 16°/4°, and n_D 1.455 at 16°; the *phenyl-carbamate* melts at 115°. 1:4-Dimethyl-2-cyclohexanone is a colourless liquid which boils at 176° (corr.) and forms a crystalline compound with sodium hydrogen sulphite and a *semicarbazone* which melts at 155°.

M. A. W.

Synthesis of Tertiary Alcohols derived from 1-Methyl-4-cyclohexanone. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1906, 142, 438—440. Compare Abstr., 1905, i, 275, 587, 706).—1:4-Dimethylcyclohexene (Abstr., 1905, i, 588) has a sp. gr. 0.8207 at 0°/4° or 0.8111 at 14°/4° and n_D 1.451 at 14°; 1-methyl-4-ethyl-4-cyclohexanol, prepared by the action of magnesium ethyl iodide on 1-methyl-4-cyclohexanone, is a liquid with an agreeable odour, boils at 89° under 20 mm. pressure, has a sp. gr. 0.9225 at 0°/4° or 0.9130 at 16°/4° and n_D 1.460 at 16°. The *acetate* boils at 197°, the *phenyl-carbamate* crystallises in brilliant needles which melt at 123°. 1-Methyl-4-ethylcyclohexene, obtained by the dehydrating action of zinc chloride, boils at 149° (corr.), has a sp. gr. 0.8278 at 0°/4° or 0.8169 at 16°/4°, n_D 1.453 at 16°, and yields 1-methyl-4-ethylcyclohexane on direct hydrogenation in the presence of reduced nickel; this hydrocarbon boils at 147° (corr.), not at 150° as originally stated (Sabatier and Senderens, Abstr., 1901, i, 459), and has a sp. gr. 0.7884 at 15°/4° and n_D 1.435 at 15°.

The chief products of the action of magnesium propyl iodide on 1-methyl-4-cyclohexanone are propylene and 1-methyl-4-cyclohexanol (compare Abstr., 1905, i, 706), together with a small quantity of 1-methyl-4-propyl-4-cyclohexanol, which is a colourless liquid smelling like camphor, and boiling at 97° under 20 mm. pressure; the corresponding cyclohexene, $C_{10}H_{18}$, boils at 168—170° (corr.), has a sp. gr. 0.8387 at 0°/4° or 0.8270 at 16°/4°, and n_D 1.455 at 16°.

1-Methyl-4-isopropyl-4-cyclohexanol, obtained in small quantity by the action of magnesium isopropyl iodide on 1-methyl-4-cyclohexanone, boils at 94° under 20 mm. pressure, and the corresponding cyclohexene boils at 166—167° and is identical with menthene.

1-Methyl-4-isoamyl-4-cyclohexanol is a colourless liquid which boils at 125° under 6 mm. pressure, has a sp. gr. 0.9043 at 0°/4° or 0.8937 at 16°/4°, and n_D 1.4615 at 16°, and yields 1-methyl-4-isoamylcyclohexene, $C_{12}H_{22}$, which is a liquid with an agreeable odour, boiling at 210° (corr.) and having a sp. gr. 0.8333 at 0°/4°, or 0.8213 at 16°/4°, and n_D 1.458 at 16°.

1-Methyl-4-sec-octyl-4-cyclohexanol is a colourless liquid with an agreeable odour, which boils at 150° under 8 mm. pressure and has a sp. gr. 0.8543 at 0°/4°.

4-Phenyl-1-methyl-4-cyclohexanol forms brilliant prisms with an aromatic odour, which melt at 64° and boil at 145° under 6 mm.

pressure, the *phenylcarbamate* forms beautiful, elongated prisms melting at 135° , and the corresponding 4-*phenyl-1-methylcyclohexene* is a colourless liquid which boils at 147° under 23 mm. pressure, has a sp. gr. 0.9846 at $0^{\circ}/4^{\circ}$ or 0.9716 at $14^{\circ}/4^{\circ}$, and n_D 1.555 at 14° .

4-*Benzyl-1-methyl-4-cyclohexanol* is a liquid with an aromatic odour, which boils at 159° under 6 mm. pressure. The *phenylcarbamate* crystallises in brilliant needles which melt at 135° . 4-*Benzyl-1-methylcyclohexene*, $C_{14}H_{18}$, is a liquid with an agreeable odour, boils at 160° under 30 mm. pressure, has a sp. gr. 0.9687 at $0^{\circ}/4^{\circ}$ or 0.9567 at $16^{\circ}/4^{\circ}$, and n_D 1.542 at 16° . M. A. W.

Nitrosophenol or Quinoneoxime. C. H. SLUITER (*Rec. Trav. chim.*, 1906, 25, 8—11).—The synthesis of nitrosophenol by Goldschmidt (*Abstr.*, 1884, 735) and that by Baeyer (*Ber.*, 1873, 6, 963), both accomplished in ionising media, support the common view that free nitrosophenol has the quinoneoxime constitution. Bridge's synthesis (*Abstr.*, 1894, i, 25), accomplished in dry ether, supports the view that it exists in the free state as a true nitroso-compound, and further evidence of this is afforded by O. Fischer and Hepp's preparation (*Abstr.*, 1887, 1114) of nitrosoaniline from nitrosophenol in a dry condition in which ionisation could not occur. The fact that pure nitrosophenol is nearly white and that its solutions in non-ionising solvents are pale yellow, whilst those in ionising solvents are green, and that the colours of the hydrated salts are green and those of the anhydrous salts red (Farmer and Hantzsch, *Abstr.*, 1900, i, 103), supports the author's view that in the free state nitrosophenol is a true nitroso-compound and that the salts have the oximino-structure.

Determination of the molecular weight of nitrosophenol, dissolved in benzene, by the ebullioscopic method showed that 50 per cent. of the substance was in the bimolecular condition, whereas in ether it appears to exist wholly in the unimolecular state. T. A. H.

***o*-Phenolsulphonates.** A. VIAL (*Bull. Soc. chim.*, 1906, [iii], 35, 159—165).—*Strontium*, *calcium*, *lead*, *silver*, *cadmium*, *copper*, *ferrous*, *aluminium*, *chromium*, *nickel*, *cobalt*, *manganese*, *magnesium*, *sodium*, *potassium*, *ammonium*, and *lithium* *o*-phenolsulphonates were prepared either by neutralising the acid with the carbonate of the appropriate metal or by double decomposition between barium *o*-phenolsulphonate and the appropriate metallic sulphate. The salts are all soluble in water, some of them also in alcohol, and all are insoluble in chloroform or benzene. The individual salts are described in detail in the original and in most cases crystallographic measurements are given.

T. A. H.

Oxidation by Fusion. CARL GRAEBE and HERMANN KRAFT (*Ber.*, 1906, 39, 794—802).—A number of substances has been oxidised by addition of lead peroxide during fusion with sodium or potassium hydroxide at 200 — 220° or at 250 — 260° . Oxidation takes place more easily in this way, and gives better yields and purer products, than by fusion with the alkali hydroxide alone. The cresols yield the corresponding hydroxybenzoic acids, the toluic acids the correspond-

ing phthalic acids. Phthalic anhydride, as also *o*-toluic acid, yields a small amount of an *acid* which melts at 270—280° and forms green, fluorescent solutions in aqueous alkali hydroxides.

Thymol remains almost unchanged at 210—220°, but at 250—260° is partially converted into a resin, the remainder undergoing complete oxidation. Eugenol yields *isoeugenol*, but is in part completely burnt or resinified.

1:3:4-Xylenol is oxidised to 4-hydroxyisophthalic acid together with traces of 4-hydroxy-3-toluic acid. 2-Hydroxyisophthalic acid is obtained by oxidation of *o*-cresotic acid; when treated with methyl sulphate in aqueous alkaline solution, it forms 2-methoxyisophthalic acid, and, when boiled with methyl alcoholic hydrochloric acid, yields the *dimethyl* ester, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{Me})_2$, melting at 72°.

The oxidation of *p*-toluenesulphonic acid leads to the formation of benzoic and *p*-hydroxybenzoic acids; the oxidation of phenol to the formation of small amounts of salicylic acid, the phenol being regained mostly unchanged.

o-Phenylbenzoic acid is obtained by the oxidation of fluorene, proto-catechuic acid in a yield of 43·6 of the theoretical by the oxidation of quinic acid, a part of which is completely oxidised. G. Y.

Preparation of 4-Chloro-2-nitroanisole. K. OEHLER (D.R.-P. 161664. Compare Abstr., 1903, i, 478).—In the action of chlorine on *o*-nitroanisole in presence of a chlorine carrier, the hydrogen chloride produced causes the hydrolysis of a large part of the ether. Perfect chlorination is, however, obtained in presence of an organic acid. Thus the addition of 15 per cent. of formic acid allows the chlorination to take place at 50—60° without any loss by hydrolysis. Acetic or chloroacetic acid may also be used. C. H. D.

Structure of the Dinitroanisoles. H. VERMEULEN (*Rec. Trav. chim.*, 1906, 25, 12—31).—In view of the unexpected results obtained by Holleman in his investigation of the nitration of the nitroanisoles (Abstr., 1903, i, 623), the author has investigated the reduction and methylation products of the dinitroanisoles. The results confirm the constitutions assigned by Henriques (Abstr., 1883, 327) to the latter substances.

It was found possible to prepare the 2:3- and 3:4-dinitroanisoles by shaking aqueous solutions of the sodium derivatives of the corresponding dinitrophenols with excess of methyl sulphate. 3:6-Dinitroanisole was obtained by warming a dry mixture of the potassium derivative of 3:6-dinitrophenol with methyl sulphate at 100°. Veratrole was prepared by adding gradually and with continuous agitation an *N*/5 solution of sodium hydroxide to a mixture of catechol and methyl sulphate previously melted together at 100°. This method of methylation is also applicable to the other dihydroxybenzenes.

2-Nitro-1:3-dimethoxybenzene, prepared by shaking the sodium derivative of 2-nitroresorcinol, dissolved in water, with a slight excess of methyl sulphate, crystallises from alcohol in long, colourless needles, melts at 130°, solidifies at 129·7° (corr.), has a sp. gr. 1·1520 at 132°, and is soluble in the usual organic solvents, but insoluble in water and light petroleum.

5-Nitro-1:3-dimethoxybenzene, similarly prepared from 5-nitro-3-methoxyphenol, crystallises from ethyl acetate in transparent, yellow needles, melts at 89° , solidifies at 87.6° , has a sp. gr. 1.169 at 132° , and is insoluble in water and light petroleum. The 3:6- and 3:4-dinitroanisoles yield the same 4-nitro-1:3-dimethoxybenzene when treated with sodium methoxide in methyl alcohol, and 2:3-dinitroanisole, under similar conditions, produces 3-nitro-1:2-dimethoxybenzene, but the dinitroanisoles having the nitro-groups in the meta-position relatively to each other do not suffer the replacement of one nitro-group by a methoxyl group under these conditions.

Ammonium sulphide does not reduce the 2:3- and 2:6-dinitroanisoles or those in which the two nitro-groups occupy the ortho-position relatively to each other. In the 2:4- and 3:6-dinitroanisoles, the NO_2 group nearer to the methoxyl group is reduced by this reagent.

The solidifying points and specific gravities of the various nitro-methoxyanilines and nitrodimethoxybenzenes prepared were determined and are tabulated in the original.

T. A. H.

Preparation of *p*-Iodoxyanisole and *p*-Iodoxyphenetole. ARTHUR LIEBRECHT (D.R.-P. 161725).—The method employed for the preparation of *o*-iodoxyanisole (Jannasch and Hinterskirch, Abstr., 1898, i, 575) is not applicable to *m*-iodoanisole.

p-Iodoanisole is acted on in aqueous suspension by chlorine or by hypochlorous acid, the final product being *p*-iodoxyanisole. The *iododichloride* forms golden-yellow crystals and undergoes spontaneous change, the chlorine migrating into the ring. The *iodoso*-compound forms white crystals and decomposes spontaneously. *p*-Iodoxyanisole crystallises from 50 per cent. acetic acid in silvery-white leaflets, explodes at 225° , and is insoluble in alcohol or ether, but dissolves in hot water. *p*-Iodoxyphenetole is similar, and also explodes at 225° . Both compounds have strong oxidising and antiseptic properties.

C. H. D.

Action of Disulphides on Organo-magnesium Haloids. Synthesis of Mixed Sulphides. HENRI WUYTS (*Bull. Soc. chim.*, 1906, [iii], 35, 166—169. Compare Abstr., 1903, i, 686, and Taboury, *ibid.*, 748).—When phenyl disulphide reacts with magnesium ethyl bromide and the reaction product is decomposed with water, phenyl ethyl sulphide and thiophenol are formed. Phenyl α -naphthyl sulphide, prepared similarly from phenyl disulphide and magnesium α -naphthyl bromide, boils at 255 — 256° under 43 mm. pressure and has a sp. gr. 1.167 at $15^{\circ}/4^{\circ}$ (compare Krafft and Bourgeois, Abstr., 1891, 76). *Ethyl isobutyl sulphide*, resulting similarly, together with ethyl mercaptan, *isobutyl chloride*, and *isobutyl alcohol*, by the interaction of ethyl disulphide with magnesium *isobutyl chloride*, is a mobile liquid of pungent odour, boils at 132 — 134° (corr.), has a sp. gr. 0.8337 at $15^{\circ}/4^{\circ}$, and n_D 1.44677.

T. A. H.

Preparation of α -Methyl- β -naphthol. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 161450).—Di- β -hydroxy- α -naphthylmethane, prepared from formaldehyde and β -naphthol, undergoes

a remarkable change when reduced with zinc dust in boiling sodium hydroxide solution, being converted into α -methyl- β -naphthol and β -naphthol, $\text{CH}_2(\text{C}_{10}\text{H}_6\cdot\text{OH})_2 + \text{H}_2 = \text{C}_{10}\text{H}_6\text{Me}\cdot\text{OH} + \text{C}_{10}\text{H}_7\cdot\text{OH}$ (compare Boehm, Abstr., 1902, i, 37). The products are separated by the addition of formaldehyde, precipitation with hydrochloric acid, and crystallisation from water.

α -Methyl- β -naphthol crystallises in needles, melts at 112° , and dissolves in alcohol, ether, or benzene. The benzoyl derivative crystallises from alcohol in long needles and melts at 117° ; the ethyl ether melts at 52° .

C. H. D.

Diphenylene Dioxide. FRITZ ULLMANN and ALBERT STEIN (*Ber.*, 1906, 39, 622—625. Compare Ullmann, Sponagel, and Stein, Abstr., 1905, i, 644).—*o*-Methoxydiphenyl ether is prepared by gradually heating a mixture of guaiacol, bromobenzene, potassium hydroxide, and copper powder at 220 — 230° , or by heating phenol with *o*-bromoanisole, potassium hydroxide, and copper powder at 190 — 215° for four hours. It crystallises from light petroleum in white needles, melts at 78° , boils at 228° , and volatilises slowly in a current of steam. When boiled with aluminium chloride in benzene solution in a reflux apparatus, it yields *o*-hydroxydiphenyl ether, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{OPh}$, which crystallises from light petroleum in colourless plates, melts at 107° , is only sparingly soluble in boiling water, but readily so in boiling alcohol or ether, and is volatile with steam; on addition of ferric chloride, the aqueous solution becomes red and opaque.

2 : 2'-Dimethoxydiphenyl ether, $\text{O}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$, is prepared by heating a mixture of guaiacol, *o*-bromoanisole, potassium hydroxide, and copper powder at 180 — 190° ; it crystallises in white leaflets, melts at 78° , boils at 330 — 331° , and when boiled with aluminium chloride and benzene forms 2 : 2'-dihydroxydiphenyl ether, $\text{O}(\text{C}_6\text{H}_4\cdot\text{OH})_2$. This crystallises from light petroleum in large, almost colourless plates, or from water in long needles, melts at 121° , and gives a blue coloration with ferric chloride.

Diphenylene dioxide, $\text{C}_6\text{H}_4\langle\text{O}\rangle\text{C}_6\text{H}_4$, is formed by heating 2 : 2'-dihydroxydiphenyl ether or 2 : 2'-dimethoxydiphenyl ether with hydrobromic acid of sp. gr. 1.49 at 180 — 190° ; it crystallises in long, colourless needles, resembling asbestos, and melts at 119° .

Di-2 : 3-naphthylene dioxide crystallises in colourless leaflets, melts at 326° , and dissolves in pyridine or toluene, forming a solution with blue fluorescence.

G. Y.

Relations between the Constitution and the Stability of the Condensation Products of Organic Bases with Substituted Hydroxybenzyl Bromides. KARL AUWERS (*Annalen*, 1906, 344, 93—141. Compare Abstr., 1896, i, 149; 1902, i, 146).—A summary of results previously obtained and an introduction to the four papers following.

The complete work embraces the preparation of seventeen substituted hydroxybenzyl bromides and the study of their condensation products with ammonia, methyl-, ethyl-, benzyl-, diethyl-, and diamylamines, aniline, methylaniline, α - and β -naphthylamines, and piperidine,

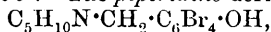
and of the quaternary salts formed with pyridine and quinoline. The condensation products are formed by the interaction of the amines with ψ -phenolic benzyl bromides in cold, with phenolic benzyl bromides in hot, ethereal or benzene solution. The stability of the condensation products towards cold and hot dilute sodium hydroxide, cold and hot anhydrous acetic acid, boiling acetic anhydride, and prolonged heating on the water-bath, has been investigated, and found to depend on the nature of the amine as well as on that of the phenol constituent. The results are given in a series of tables. G. Y.

Condensation Products of Organic Bases with Phenols and ψ -Phenols of the Cresol Series. KARL AUWERS and O. SCHRÖTER (*Annalen*, 1906, 344, 141—170. See preceding abstract).—3:5-Dibromo-2-hydroxybenzyl bromide (Auwers and Büttner, *Abstr.*, 1899, i, 36) is prepared best by heating *o*-cresol with bromine at 115—120°. The piperidine derivative remains unchanged when boiled with 10 per cent. sodium hydroxide or glacial acetic acid for one hour, or when heated alone on the water-bath, but when boiled with acetic anhydride yields piperidine and dibromosaligenin diacetate, melting at 70—71°. The methylamine derivative, $\text{NMe}(\text{CH}_2 \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{OH})_2$, is not decomposed when heated at 100° or when boiled with dilute sodium hydroxide or glacial acetic acid, and yields only a small amount of methylamine when boiled with acetic anhydride.

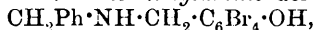
The benzylamine derivative, $\text{CH}_2\text{Ph} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{OH}$, crystallises from methyl alcohol in silvery needles, melts at 129—130°, is stable to boiling dilute sodium hydroxide, but yields a small amount of benzylamine when boiled with glacial acetic acid, and is decomposed completely by boiling acetic anhydride.

The diamylamine derivative, $\text{N}(\text{C}_5\text{H}_{11})_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{OH}$, is isolated in the form of its hydrochloride, $\text{C}_{17}\text{H}_{27}\text{ONBr}_2 \cdot \text{HCl}$; it is decomposed by 5 per cent. aqueous sodium hydroxide, slightly at the laboratory temperature, to a greater extent when heated, and when boiled with glacial acetic acid or acetic anhydride yields dibromosaligenin mono- and di-acetate respectively. Dibromosaligenin monoacetate, melting at 110—112°, is soluble in dilute sodium hydroxide and remains unchanged when boiled with methyl alcohol or a mixture of methyl alcohol or water and acetone.

Tetrabromo-o-hydroxybenzyl bromide, $\text{OH} \cdot \text{C}_6\text{Br}_4 \cdot \text{CH}_2\text{Br}$, is prepared by brominating *o*-cresol at the laboratory temperature and heating the product with bromine in a sealed tube at 100°; it crystallises from glacial acetic acid and melts at 156°. The methylamine derivative, $\text{NMe}(\text{CH}_2 \cdot \text{C}_6\text{Br}_4 \cdot \text{OH})_2$, melts at 205—207°, and when boiled with acetic anhydride forms a diacetyl derivative, $\text{NMe}(\text{CH}_2 \cdot \text{C}_6\text{Br}_4 \cdot \text{OAc})_2$, which melts at 145—150°. The piperidine derivative,

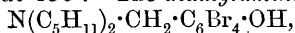


forms a yellow powder, melts at 106—108°, and when boiled with acetic anhydride yields tetrabromosaligenin diacetate, $\text{C}_7\text{H}_2\text{Br}_4(\text{OAc})_2$, which melts at 138—139°. The benzylamine derivative,



crystallises in leaflets, melts at 170—171°, and is decomposed only slightly by boiling 5 per cent. sodium hydroxide or by cold glacial acetic

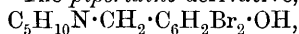
acid, but when boiled with glacial acetic acid yields *tetrabromosaligenin acetate*, $\text{OH}\cdot\text{C}_6\text{Br}_4\cdot\text{CH}_2\cdot\text{OAc}$, which melts at 133° and remains unchanged when boiled with methyl alcohol or aqueous acetone. When boiled with acetic anhydride, the benzylamine compound forms the *acetyl* derivative, $\text{CH}_2\text{Ph}\cdot\text{NAc}\cdot\text{C}_6\text{Br}_4\cdot\text{OH}$, which crystallises in glistening prisms and melts at 150° . The *diamylamine* derivative,



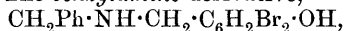
is an oil which forms a solid *hydrochloride*, $\text{C}_{17}\text{H}_{23}\text{ONBr}_4\cdot\text{HCl}$; it is decomposed only slightly by boiling dilute sodium hydroxide or cold glacial acetic acid, but yields *tetrabromosaligenin monoacetate* when boiled with glacial acetic acid, or the diacetate when boiled with acetic anhydride.

Tetrabromo-m-hydroxybenzyl bromide, $\text{OH}\cdot\text{C}_6\text{Br}_4\cdot\text{CH}_2\text{Br}$, melting at 137° (Auwers and Anselmino, Abstr., 1900, i, 159), is prepared by heating *tetrabromo-m-cresol* with bromine in a sealed tube at 100° . The *piperidine* derivative, $\text{C}_{12}\text{H}_{13}\text{ONBr}_4$, crystallises from benzene in slender, white needles, melts at 193° , yields only traces of piperidine when boiled with dilute sodium hydroxide or glacial acetic acid, and is converted by boiling acetic anhydride into the *acetyl* derivative, $\text{C}_5\text{H}_{10}\text{N}\cdot\text{CH}_2\cdot\text{C}_6\text{Br}_4\cdot\text{OAc}$, which melts at $129\text{--}130^\circ$. The *methylamine* derivative, $\text{NMe}(\text{CH}_2\cdot\text{C}_6\text{Br}_4\cdot\text{OH})_2$, resembles the piperidine derivative, but could not be obtained in a state of purity. The *diamylamine* derivative, $\text{N}(\text{C}_5\text{H}_{11})_2\cdot\text{CH}_2\cdot\text{C}_6\text{Br}_4\cdot\text{OH}$, crystallises in matted, slender needles, melts at $167\text{--}168^\circ$, is only slightly decomposed by boiling dilute sodium hydroxide or glacial acetic acid, and when boiled with acetic anhydride yields the *acetate*, $\text{N}(\text{C}_5\text{H}_{11})_2\cdot\text{CH}_2\cdot\text{C}_6\text{Br}_4\cdot\text{OAc}$, which is hydrolysed by boiling alcoholic sodium hydroxide.

The *methylamine* derivative, $\text{NMe}(\text{CH}_2\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{OH})_2$, formed from 3:5-dibromo-4-hydroxybenzyl bromide and methylamine, is obtained as a crystalline powder, melts at 180° , is decomposed by boiling glacial acetic acid with formation of methylamine and 3:5-dibromo-4-hydroxybenzyl acetate, melting at 115° , and when boiled with acetic anhydride yields the diacetate, melting at 68° (Auwers and Daecke, Abstr., 1900, i, 164). The *piperidine* derivative,



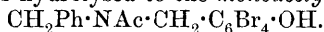
forms a yellow, micro-crystalline powder, melts at 183° , and, in its behaviour to acetic acid and acetic anhydride, resembles the methylamine derivative. The *benzylamine* derivative,



is isolated in the form of its *hydrochloride*, $\text{C}_{14}\text{H}_{14}\text{ONClBr}_2$; it yields a small amount of benzylamine when boiled with dilute sodium hydroxide, is completely decomposed by boiling glacial acetic acid containing sodium acetate, with formation of benzylamine and 3:5:3':5'-tetrabromo-4:4'-dihydroxydiphenylmethane, and when boiled with acetic anhydride yields a resinous, nitrogenous product, which is insoluble in aqueous alkali hydroxides. The *diamylamine* derivative, $\text{N}(\text{C}_5\text{H}_{11})_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{OH}$, is obtained as a glutinous, friable mass, which melts at $70\text{--}97^\circ$ and decomposes when recrystallised or when heated on the water-bath; it is decomposed to the extent of about 25 per cent. when boiled with dilute sodium hydroxide, or completely with formation of 3:5:3':5'-tetrabromo-4:4'-dihydroxydiphenylmethane,

or of its acetyl derivative respectively, when boiled with glacial acetic acid or acetic anhydride.

The *methylamine* derivative, $\text{NMe}(\text{CH}_2\cdot\text{C}_6\text{Br}_4\cdot\text{OH})_2$, prepared from tetrabromo-*p*-hydroxybenzyl bromide, crystallises in slender, white needles, melts at 215° , and is decomposed by boiling glacial acetic acid with formation of the monoacetyl or by boiling acetic anhydride with formation of the diacetyl derivative of tetrabromo-*p*-hydroxybenzyl alcohol (Zincke and Wiederhold, Abstr., 1902, i, 285). The *piperidine* derivative, $\text{C}_5\text{H}_{10}\text{N}\cdot\text{CH}_2\cdot\text{C}_6\text{Br}_4\cdot\text{OH}$, crystallises in white scales, melts at about 185° , and behaves towards acetic acid and acetic anhydride in the same way as the methylamine derivative. The *benzylamine* derivative, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{Br}_4\cdot\text{OH}$, melts at 163° , yields only traces of benzylamine when boiled with dilute sodium hydroxide, and is converted by boiling glacial acetic acid into octabromo-4 : 4'-dihydroxydiphenylmethane, melting at $276\text{--}277^\circ$ (Zincke and Böttcher, this vol., i, 166); its *diacetyl* derivative, $\text{CH}_2\text{Ph}\cdot\text{NAc}\cdot\text{CH}_2\cdot\text{C}_6\text{Br}_4\cdot\text{OAc}$, formed by boiling the benzylamine compound with acetic anhydride, crystallises in stout needles, melts at $146\text{--}147^\circ$, and when boiled with alcoholic sodium hydroxide is hydrolysed to the *monoacetyl* derivative,



The *diamylamine* derivative, $\text{N}(\text{C}_5\text{H}_{11})_2\cdot\text{CH}_2\cdot\text{C}_6\text{Br}_4\cdot\text{OH}$, is obtained as a resin, decomposes slowly when heated on the water-bath, and yields diamylamine and octabromodi-*p*-hydroxyphenylmethane when boiled with dilute sodium hydroxide or glacial acetic acid. The base, when boiled with acetic anhydride, yields *octabromodi-p-acetoxyphenylmethane*, $\text{C}_{17}\text{H}_8\text{O}_4\text{Br}_8$, melting at $276\text{--}277^\circ$.

With the exception of the diamylamine derivatives from 3 : 5-dibromo- and tetrabromo-hydroxybenzyl bromides, the bases described in this paper remain unchanged when heated on the water-bath for one hour.

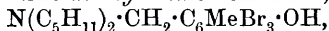
G. Y.

Condensation Products of Organic Bases with Phenols and ψ -Phenols of the Xylenol and Hemimellithenol Series. KARL AUWERS, C. KIPKE, A. SCHRENK, and O. SCHRÖTER (*Annalen*, 1906, 344, 171—193. Compare preceding abstract).—3 : 5-Dibromo-1 : 2 : 4-xylenol, $\text{OH}\cdot\text{C}_6\text{HMe}_2\text{Br}_2$, is prepared by the action of bromine on 1 : 2 : 4-xylenol in concentrated glacial acetic acid solution; it crystallises in slender, white needles, melts at $39\text{--}40^\circ$, boils at about 300° , and is readily soluble in organic solvents. The *benzoate*, $\text{C}_{15}\text{H}_{12}\text{O}_2\text{Br}_2$, crystallises in slender needles and melts at $125\text{--}126^\circ$. ω : 3 : 5-Tribromo-1 : 2 : 4-xylenol, $\text{C}_8\text{H}_7\text{OBr}_3$, is formed by adding bromine to 3 : 5-dibromo-1 : 2 : 4-xylenol heated to $120\text{--}130^\circ$; it crystallises in slender needles and small, nodular aggregates, melts at $90\text{--}97^\circ$, and is insoluble in aqueous alkali hydroxides.

ω : 3 : 5 : 6-Tetrabromo-1 : 2 : 4-xylenol, melting at 173° (Auwers and Erggelet, Abstr., 1900, i, 97), is prepared best by heating tribromoxylenol with half its weight of bromine in a sealed tube at 100° . The *piperidine* derivative, $\text{C}_5\text{H}_{10}\text{N}\cdot\text{CH}_2\cdot\text{C}_6\text{MeBr}_3\cdot\text{OH}$, crystallises in stout, nacreous leaflets, melts at $159\cdot5\text{--}160^\circ$, is readily soluble in glacial acetic acid, and is hydrolysed only partially by boiling dilute sodium hydroxide, but almost completely by boiling glacial acetic acid; when boiled with acetic anhydride, it yields the diacetyl derivative of

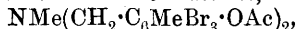
3:5:6-tribromo- ω :4-dihydroxy-1:2-xylene, melting at 135—137° (Auwers and Erggelet, *loc. cit.*).

The *methylamine* derivative, $\text{NMe}(\text{CH}_2 \cdot \text{C}_6\text{MeBr}_3 \cdot \text{OH})_2$, formed from ω :2:5:6-tetrabromo-1:3:4 xylenol (Auwers and Campenhausen, *Abstr.*, 1896, i, 424), softens at 155°, melts at 161°, is readily soluble in benzene, or moderately so in ethyl acetate, chloroform, or alcohol, and when boiled with glacial acetic acid yields methylamine and the monoacetyl derivative of tribromo-4-hydroxy-1:3-xylyl alcohol, melting at 153—154° (Auwers and Ziegler, *Abstr.*, 1897, i, 33). The base is decomposed also by boiling acetic anhydride, with formation of 2:5:6-tribromo- ω :4-diacetoxy-1:3-xylene, $\text{OAc} \cdot \text{C}_6\text{MeBr}_3 \cdot \text{CH}_2 \cdot \text{OAc}$, which crystallises in needles and melts at 136—136.5°. The piperidine derivative, $\text{C}_5\text{H}_{10}\text{N} \cdot \text{CH}_2 \cdot \text{C}_6\text{MeBr}_3 \cdot \text{OH}$, which melts at 157° (Auwers and Ziegler, *loc. cit.*), is decomposed in the same way as the methylamine derivative by acetic acid and acetic anhydride. The *benzylamine* derivative, $\text{CH}_2\text{Ph} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{C}_6\text{MeBr}_3 \cdot \text{OH}$, crystallises in short, glistening prisms, melts at 138°, and when boiled with glacial acetic acid yields the monoacetate of tribromo-4-hydroxy-1:3-xylyl alcohol. The *diacetyl* derivative, $\text{CH}_2\text{Ph} \cdot \text{N} \cdot \text{Ac} \cdot \text{CH}_2 \cdot \text{C}_6\text{MeBr}_3 \cdot \text{OAc}$, formed by boiling the base with acetic anhydride, crystallises in microscopic leaflets and melts at 118—120°. The *diamylamine* derivative,



crystallises in matted, small needles, melts at 99—100°, does not give the potassium test for nitrogen, decomposes slightly on prolonged heating on the water-bath, and yields only small quantities of diamylamine when boiled with aqueous sodium hydroxide; when boiled with acetic acid and with acetic anhydride, the base yields the mono- and di-acetates of tribromo-4-hydroxy-1:3-xylyl alcohol respectively. When boiled with methyl alcohol, the monoacetate is converted into the monomethyl ether, $\text{OH} \cdot \text{C}_6\text{MeBr}_3 \cdot \text{CH}_2 \cdot \text{OMe}$.

ω :2:5:6-Tetrabromo-3-hydroxy-*p*-xylene (Auwers and Anselmino, *Abstr.*, 1900, i, 159; Auwers and Ebner, *ibid.*, 161) is prepared best by the action of an excess of bromine and water on tetrabromo- ψ -cumenol. The *methylamine* derivative, $\text{NMe}(\text{CH}_2 \cdot \text{C}_6\text{MeBr}_3 \cdot \text{OH})_2$, is obtained as a white, amorphous powder, melts at 151—152°, and when heated alone on the water-bath, or digested at the laboratory temperature for eighteen hours, or boiled for one hour with aqueous sodium hydroxide, yields hexabromodi-*m*-hydroxydi-*p*-tolylmethane; when boiled with acetic anhydride, the base forms the *diacetate*,



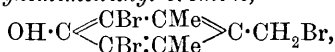
which crystallises in thin, colourless, rhombic leaflets and melts at 132—133°. The *piperidine* derivative, $\text{C}_5\text{H}_{10}\text{N} \cdot \text{CH}_2 \cdot \text{C}_6\text{MeBr}_3 \cdot \text{OH}$, crystallises in colourless plates, melts at 116—117°, and is decomposed by boiling dilute sodium hydroxide in one hour to the extent of 22.3—24.8 per cent., yielding a *product* which melts at a high temperature and is soluble in aqueous alkali hydroxides; when boiled with acetic anhydride, the base forms the *acetate*, $\text{C}_{15}\text{H}_{18}\text{O}_2\text{NBr}_3$, which crystallises in slender, white needles and melts at 92—94°. The *diamylamine* derivative, $\text{N}(\text{C}_5\text{H}_{11})_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{MeBr}_3 \cdot \text{OH}$, crystallises in glistening, white needles, melts at 81—81.5°, and when boiled with dilute sodium hydroxide or glacial acetic acid is rapidly converted

into hexabromodi-*m*-hydroxydi-*p*-tolylmethane, the *acetate* of which is formed by boiling the base with acetic anhydride; it melts at 260° and is insoluble in dilute alkali hydroxides.

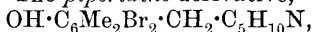
Hexabromodi-m-hydroxydi-p-tolylmethane, $\text{CH}_2(\text{C}_6\text{MeBr}_3\cdot\text{OH})_2$, crystallises from a mixture of benzene and toluene in small, white scales, melts at 251°, and is moderately soluble in alcohol or glacial acetic acid.

2:5:6-Tribromo-3-hydroxy-p-xylyl acetate, $\text{OH}\cdot\text{C}_6\text{MeBr}_3\cdot\text{CH}_2\cdot\text{OAc}$, formed by boiling the tetrabromo-compound with sodium acetate in acetic acid solution, crystallises in slender, light yellow prisms, melts at 132—134°, and remains unchanged when boiled with methyl alcohol or aqueous acetone, or when dissolved in dilute sodium hydroxide, and is quickly reprecipitated by adding an acid.

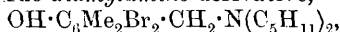
Dibromo-p-hydroxyhemimellithyl bromide,



melts at 140—142°. The *piperidine* derivative,



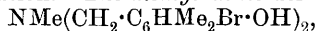
crystallises in sheaves of long needles, melts at 110°, decomposes gradually with evolution of piperidine when heated on the water-bath, and is decomposed to only a slight extent by cold glacial acetic acid or aqueous sodium hydroxide, but completely with formation of tetrabromodihydroxytetramethyldiphenylmethane when boiled in alkaline solution. The *diamylamine* derivative,



melts and decomposes at 81° and is decomposed rapidly by boiling aqueous sodium hydroxide.

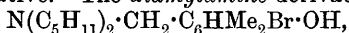
3:5:3':5'-Tetrabromo-4:4'-dihydroxy-2:6:2':6'-tetramethyldiphenylmethane, $\text{CH}_2(\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{OH})_2$, crystallises in matted, slender needles and melts at 246°. With the exception of the diamylamine derivative of 2:5:6-tribromo-4-hydroxy-*m*-xylyl bromide, and the methylamine derivative of 2:5:6-tribromo-3-hydroxy-*p*-xylyl bromide, and the piperidine and diamylamine derivatives of dibromo-*p*-hydroxyhemimellithyl bromide, the bases described above remain unchanged when heated on the water-bath for one hour. G. Y.

Condensation Products of Organic Bases with Phenols and ψ -Phenols of the ψ -Cumenol Series. KARL AUWERS and C. KIPKE (*Annalen*, 1906, 344, 194—226. Compare preceding abstracts).—3-Bromo-2-hydroxy- ψ -cumyl bromide, melting at 66—67° (Auwers and Rovaart, *Abstr.*, 1899, i, 34), is formed by bromination of *o*-hydroxy- ψ -cumyl alcohol (Auwers and Anselmino, *Abstr.*, 1902, i, 214) in ether-chloroform solution. The *methylamine* derivative,



crystallises in glistening, flat plates, melts at 116—117°, and when boiled with acetic anhydride is partially decomposed with formation of methylamine. The *piperidine* derivative, $\text{C}_5\text{H}_{10}\text{N}\cdot\text{CH}_2\cdot\text{C}_6\text{HMe}_2\text{Br}\cdot\text{OH}$, crystallises in long, transparent needles, melts at 87—88°, and when boiled with acetic anhydride yields the *diacetate* of 3-bromo-2-hydroxy- ψ -cumyl alcohol, $\text{OAc}\cdot\text{C}_6\text{HMe}_2\text{Br}\cdot\text{CH}_2\cdot\text{OAc}$, which is formed also by boiling the bromide with sodium acetate and acetic anhydride. It

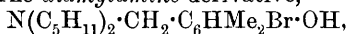
crystallises in slender needles and melts at 51—52°. The *benzylamine* derivative, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{CH}_2\cdot\text{C}_6\text{HMe}_2\text{Br}\cdot\text{OH})_2$, crystallises in slender needles, melts at 147—148°, and is decomposed by boiling acetic anhydride in the same manner as, but more completely than, the methylamine derivative. The *diamylamine* derivative,



is an oil which is hydrolysed with formation of diamylamine by glacial acetic acid at the laboratory temperature, and when boiled with acetic anhydride yields the diacetate of 3-bromo-2-hydroxy- ψ -cumyl alcohol.

The *piperidine* derivative, $\text{CMe}\begin{matrix} \text{C}(\text{OH})\cdot\text{CBr} \\ \text{CBr}=\text{CMe} \end{matrix}\text{C}\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_{10}$, formed from 3:6-dibromo-5-hydroxy- ψ -cumyl bromide, melting at 128° (Auwers and Maas, Abstr., 1900, i, 162), crystallises in long, flat needles, melts at 68—69°, is readily soluble in organic solvents, and remains unchanged when boiled with 5 per cent. aqueous sodium hydroxide.

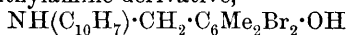
The *methylamine* derivative, $\text{NMe}(\text{CH}_2\cdot\text{C}_6\text{HMe}_2\text{Br}\cdot\text{OH})_2$, formed from 3-bromo-4-hydroxy- ψ -cumyl bromide, melting at 81° (Auwers and Ercklentz, Abstr., 1899, i, 35), crystallises in plates or stellate aggregates of needles, melts at 150—151°, when boiled with dilute sodium hydroxide yields 3:3'-dibromo-4:4'-dihydroxy-2:5:2':5'-tetramethyldiphenylmethane, melting at 151—153° (Auwers, Abstr., 1903, i, 622), and is converted by boiling with glacial acetic acid into the monoacetate, with acetic anhydride into the diacetate of bromo-*p*-hydroxy- ψ -cumyl alcohol (Auwers and Ercklentz, *loc. cit.*). 3-Bromo-4-hydroxy- ψ -cumylpiperidine (Auwers and Ercklentz, *loc. cit.*) yields the diphenylmethane derivative when heated on the water-bath or when boiled with aqueous sodium hydroxide, and when boiled with glacial acetic acid or acetic anhydride yields the mono- or di-acetate, respectively, of bromo-*p*-hydroxy- ψ -cumyl alcohol. The *benzylamine* derivative, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{CH}_2\cdot\text{C}_6\text{HMe}_2\text{Br}\cdot\text{OH})_2$, crystallises in stellate aggregates of needles, melts at 123—133°, and when boiled with dilute sodium hydroxide, glacial acetic acid, and acetic anhydride yields the diphenylmethane and the mono- and di-acetates respectively of the ψ -cumyl alcohol. The *diamylamine* derivative,



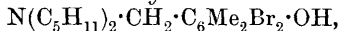
is isolated in the form of its hydrochloride, $\text{C}_{19}\text{H}_{32}\text{ONBr}\cdot\text{HCl}$; the base decomposes and forms the diphenylmethane derivative when heated on the water-bath or boiled with dilute sodium hydroxide, or less completely when shaken with cold aqueous sodium hydroxide; it is decomposed by boiling glacial acetic acid, or, with formation of the diacetate of the ψ -cumyl alcohol, by boiling acetic anhydride.

The following bases are prepared from 3:6-dibromo-4-hydroxy- ψ -cumyl bromide (Auwers and Marwedel, Abstr., 1896, i, 149). The ammonia derivative, $\text{N}(\text{CH}_2\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{OH})_3$ (Auwers and Hof, Abstr., 1896, i, 421), is partially decomposed by boiling dilute sodium hydroxide with formation of the diphenylmethane derivative, $\text{CH}_2(\text{C}_6\text{Me}_2\text{Br}\cdot\text{OH})_2$, melting at 232°, and when boiled with glacial acetic acid forms a solution which, on cooling, deposits the diphenylmethane derivative, but if diluted with water whilst hot yields the monoacetate of 3:6-dibromo-4-hydroxy- ψ -cumyl alcohol, melting at

112—115°; when boiled with acetic anhydride, the tertiary base is converted into the diacetate of dibromo-4-hydroxy- ψ -cumyl alcohol, together with a small quantity of a nitrogenous *product*. The methylamine derivative (Auwers and Hof, *loc. cit.*) is decomposed by boiling 10 per cent. sodium hydroxide with formation of the diphenylmethane derivative melting at 232°, but remains almost unchanged when boiled with 2½ per cent. aqueous sodium hydroxide; it is decomposed by glacial acetic acid only slowly at the laboratory temperature, quickly when boiled, with formation of the monoacetate of the ψ -cumyl alcohol, or by boiling acetic anhydride, with formation of the diacetate of the ψ -cumyl alcohol. When boiled with acetic anhydride, the hydrobromide of the methylamine base yields 3:6-dibromo-4-acetoxy- ψ -cumyl bromide melting at 161°. The ethylamine derivative (Auwers and Hof, *loc. cit.*) is decomposed by aqueous sodium hydroxide, glacial acetic acid, and acetic anhydride in the same way and with formation of the same products as is the methylamine derivative; when boiled with absolute alcohol, the base yields ethylamine and 3:6-dibromo-4-hydroxy- ψ -cumyl ethyl ether, melting at 85—87°. The *benzylamine* derivative, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{CH}_2\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{OH})_2$, crystallises in broad needles, melts at 183—184°, and when boiled with 10 per cent. aqueous sodium hydroxide, glacial acetic acid, and acetic anhydride, yields benzylamine and the diphenylmethane derivative melting at 232°, and the mono- and di-acetate of dibromo-4-hydroxy- ψ -cumyl alcohol respectively. A second preparation of the base was much more stable towards cold glacial acetic acid or boiling dilute sodium hydroxide. The β -naphthylamine derivative,

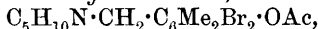


(Auwers and Senter, *Abstr.*, 1896, i, 423), remains unchanged when boiled with 5 per cent. aqueous sodium hydroxide; the action of boiling glacial acetic acid on the base leads to the formation of the *mono-acetyl* derivative, $\text{N}(\text{C}_{10}\text{H}_7)\text{Ac}\cdot\text{CH}_2\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{OH}$, which crystallises in strongly refracting, monoclinic prisms and melts at 226—227·5°. The *diacetyl* derivative, $\text{N}(\text{C}_{10}\text{H}_7)\text{Ac}\cdot\text{CH}_2\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{OAc}$, formed by boiling the base with acetic anhydride, crystallises in small, white needles and melts at 148·5—151·5°. The α -naphthylamine derivative, $\text{C}_{10}\text{H}_7\text{ONBr}_2$, crystallises in small, glistening, slightly brown or violet needles, melts at 196—197°, and is slightly less stable than the β -naphthylamine derivative. The diethylamine derivative (Auwers and Hof, *loc. cit.*) yields diethylamine and the diphenylmethane derivative melting at 232° when heated on the water-bath or when boiled with 10 per cent. aqueous sodium hydroxide or with glacial acetic acid; the action of boiling acetic anhydride on the base leads to the formation of the diacetate of the ψ -cumyl alcohol, on the hydrobromide of the base, to the formation of the acetate of dibromo-4-hydroxy- ψ -cumyl bromide. The *diamylamine* derivative,



melts at 43—45°, decomposes with formation of the diphenylmethane derivative when heated on the water-bath or when shaken with cold dilute sodium hydroxide or glacial acetic acid, and when boiled with glacial acetic acid yields the monoacetate, or with acetic anhydride the diacetate of dibromo-4-hydroxy- ψ -cumyl alcohol. The methylaniline

derivative (Auwers and Senter, *loc. cit.*) is decomposed with formation of the diphenylmethane derivative, slowly at the laboratory temperature, quickly when boiled with sodium hydroxide; the action of glacial acetic acid on the base leads to the formation of mixtures of the unchanged base with the diphenylmethane derivative; when boiled with acetic anhydride, the base yields the diacetate of dibromo-4-hydroxy- ψ -cumyl alcohol. The piperidine derivative (Auwers and Marwedel, *loc. cit.*) is almost completely decomposed by boiling 10 per cent. aqueous sodium hydroxide with formation of piperidine and the diphenylmethane derivative; when boiled with glacial acetic acid, it yields the diacetate melting at 113—115°, together with a small quantity of the diphenylmethane derivative; the *acetyl* derivative,



formed by boiling the base with acetic anhydride, crystallises in fern-like aggregates of needles and melts at 97°. The piperidine base yields the diphenylmethane derivative also when heated on the water-bath and when boiled with toluene or with alcohol. The quaternary bromide formed from 3:6-dibromo-4-hydroxy- ψ -cumyl bromide and pyridine (Auwers and Avery, *Abstr.*, 1896, i, 150) is decomposed by boiling glacial acetic acid with formation of the monoacetate melting at 112—115°, or by boiling acetic anhydride with formation of the acetate of dibromo-4-hydroxy- ψ -cumyl bromide. The quaternary bromide formed with quinoline (Auwers and Senter, *loc. cit.*) is decomposed by boiling aqueous sodium hydroxide with formation of the diphenylmethane derivative or by glacial acetic acid or acetic anhydride in the same way as the pyridine bromide. The aniline derivative (Auwers and Marwedel, *loc. cit.*) is not decomposed by heating on the water-bath or by boiling with dilute sodium hydroxide; when boiled with glacial acetic acid, it forms the acetate melting at 224°, or, with acetic anhydride, the diacetate melting at 140° (Auwers and Anselmino, *Abstr.*, 1904, i, 736).

The *methylamine* derivative, $\text{NMe}(\text{CH}_2\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{OMe})_3$, of 3:6-dibromo-4-methoxy- ψ -cumyl bromide (Auwers and Reichel, *Abstr.*, 1904, i, 997) melts at 149° and remains unchanged when boiled with dilute sodium hydroxide, glacial acetic acid, or acetic anhydride. The *diamylamine* derivative, $\text{N}(\text{C}_5\text{H}_{11})_2\cdot\text{CH}_2\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{OMe}$, melts at 158° and resembles the methylamine derivative in its stability.

The diamylamine derivative, $\text{N}(\text{C}_5\text{H}_{11})_2\cdot\text{CH}_2\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{OAc}$, formed from dibromo-*p*-acetoxy- ψ -cumyl bromide, separates from methyl alcohol in small, white crystals, melts at 45—46°, remains unchanged when boiled with glacial acetic acid or acetic anhydride, and is only slightly hydrolysed by boiling aqueous sodium hydroxide.

The *quaternary bromide*, $\text{OMe}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_5\text{Br}$, formed from pyridine and dibromo-4-methoxy- ψ -cumyl bromide, crystallises from benzene, melts at 218—219°, and is decomposed into its components when boiled with glacial acetic acid or acetic anhydride.

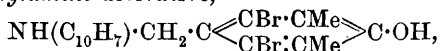
With the exception of the piperidine and diamylamine derivatives of 3-bromo-4-hydroxy- ψ -cumyl bromide, and the diethylamine, diamylamine, methylaniline, and piperidine derivatives of 3:6-dibromo-4-hydroxy- ψ -cumyl bromide, the bases described in this paper remain unchanged when heated on the water-bath.

G. Y.

Condensation Products of Organic Bases with ψ -Phenols of the Mesityl Series. KARL AUWERS and A. SCHRENK (*Annalen*, 1906, 344, 227—255. Compare preceding abstracts).—The *ammonia* derivative, $N(CH_2 \cdot C_6Me_2Br_2 \cdot OH)_3$, formed by the action of ammonia on dibromo-*p*-hydroxymesityl bromide (Auwers and Allendorff, *Abstr.*, 1899, i, 32), is obtained as a white, amorphous mass, which melts and decomposes at 250° , and is decomposed by boiling 10 per cent. aqueous sodium hydroxide, with formation of ammonia and tetrabromodihydroxytetramethyldiphenylmethane, melting at 232° , but yields only traces of ammonia when boiled with glacial acetic acid; the *triacetate*, $N(CH_2 \cdot C_6Me_2Br_2 \cdot OAc)_3$, formed by boiling the base with acetic anhydride, crystallises in small, colourless prisms and melts at 223 — 224° . The *methylamine* derivative, $NMe(CH_2 \cdot C_6Me_2Br_2 \cdot OH)_2$, melts at 154° and is partially decomposed by boiling dilute sodium hydroxide, with formation of the diphenylmethane derivative, which is formed together with the *acetate*, $OAc \cdot CH_2 \cdot C \begin{smallmatrix} \swarrow CBr \cdot CMe \\ \searrow CBr \cdot CMe \end{smallmatrix} \cdot C \cdot OH$, melting at 165 — 167° , when the base is treated with glacial acetic acid at the laboratory temperature; the action (1) of boiling glacial acetic acid on the base leads to the formation of the diacetate of dibromo-*p*-hydroxymesityl alcohol, together with a small quantity of the diphenylmethane derivative; (2) of boiling acetic anhydride to the formation of the diacetate and a small amount of a *product* which is insoluble in aqueous alkali hydroxides, contains nitrogen, and is probably the acetyl derivative of the base. When boiled with acetic anhydride, the hydrobromide of the methylamine base yields dibromo-*p*-acetoxy-mesityl bromide melting at 150 — 151° . Dibromo-*p*-hydroxymesityl ethyl ether, melting at 145 — 147° , is formed when the methylamine base is boiled with alcohol.

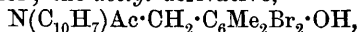
The *ethylamine* derivative, $NEt(CH_2 \cdot C_6Me_2Br_2 \cdot OH)_2$, crystallises in small, white needles, melts at 152° , yields ethylamine and the diphenylmethane derivative when heated on the water-bath, is converted completely into the diphenylmethane derivative by dilute aqueous sodium hydroxide at the laboratory temperature in twenty-four hours, and when treated with glacial acetic acid and acetic anhydride yields the same derivatives as does the methylamine derivative. The *benzylamine* derivative, $CH_2Ph \cdot NH \cdot CH_2 \cdot C \begin{smallmatrix} \swarrow CBr \cdot CMe \\ \searrow CBr \cdot CMe \end{smallmatrix} \cdot C \cdot OH$, crystallises in glistening prisms, melts at 127° , remains almost unchanged when heated on the water-bath, is partially decomposed by boiling aqueous sodium hydroxide with formation of benzylamine and the diphenylmethane derivative, and yields benzylamine and a mixture of products when boiled with glacial acetic acid; the *diacetyl* derivative, $CH_2Ph \cdot NAc \cdot CH_2 \cdot C_6Me_2Br_2 \cdot OAc$, formed by boiling the base with acetic anhydride, crystallises in needles and melts at 117 — 118° .

The β -*naphthylamine* derivative,



crystallises in delicate leaflets, melts at 233° , and remains unchanged when heated on the water-bath or boiled with aqueous sodium

hydroxide or alcohol; the *acetyl* derivative,



formed by boiling the base with glacial acetic acid, crystallises in small, glistening prisms and melts at 207—208°, and the *diacetyl* derivative, $\text{C}_{23}\text{H}_{21}\text{O}_3\text{NBr}_2$, formed by boiling the base with acetic anhydride, crystallises in light yellow needles and melts at 182—184°. The *diethylamine* derivative, $\text{NEt}_3\cdot\text{CH}_2\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{OH}$, crystallises in nodular aggregates of white needles, melts at 115—116°, and decomposes slowly at the laboratory temperature, quickly when heated on the water-bath; it is completely decomposed by boiling aqueous sodium hydroxide, or, with formation of the diphenylmethane derivative and the mono- and di-acetates of dibromo-*p*-hydroxymesityl alcohol, when boiled with acetic acid; the diacetate is formed by boiling the base with acetic anhydride. When boiled with alcohol, the diethylamine base yields dibromo-*p*-hydroxymesityl ethyl ether.

The *diamylamine* derivative, $\text{N}(\text{C}_5\text{H}_{11})_2\cdot\text{CH}_2\langle\text{CBr}\cdot\text{CMe}\rangle\text{C}\cdot\text{OH}$,

crystallises in stellate aggregates of slender prisms, melts at 94°, and decomposes with formation of the diphenylmethane derivative when heated on the water-bath, or when recrystallised from hot solvents, or when boiled with dilute sodium hydroxide. The base yields the diphenylmethane derivative when treated with cold glacial acetic acid, or dibromo-*p*-acetoxymesityl acetate when boiled with the acid; the action of boiling acetic anhydride on the base leads to the formation of the diacetates of dibromo-*p*-hydroxymesityl alcohol and the diphenylmethane derivative, melting at 159—160° and 244° respectively.

The methylaniline derivative, $\text{NMePh}\cdot\text{CH}_2\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{OH}$, melts at 103—104°, decomposes with formation of methylaniline when heated on the water-bath, is decomposed only partially, forming the diphenylmethane derivative, when boiled with dilute sodium hydroxide, and yields the mono- and di-acetates of dibromo-*p*-hydroxymesityl alcohol when boiled with glacial acetic acid or acetic anhydride.

The piperidine derivative, $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_{10}$, decomposes gradually, forming the diphenylmethane derivative when heated on the water-bath or when boiled with dilute sodium hydroxide, and yields the diacetate of dibromo-*p*-hydroxymesityl alcohol when boiled with glacial acetic acid or acetic anhydride.

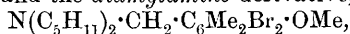
The quaternary *bromide*, $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_5\text{Br}$, melts at 260°, and when digested with cold dilute sodium hydroxide or carbonate yields the yellow substance, $\text{C}_9\text{H}_8\text{OBr}_2\cdot\text{C}_5\text{NH}_5\cdot\text{H}_2\text{O}$, melting at 242—245° (Auwers and Avery, Abstr., 1896, i, 150). When boiled with dilute sodium hydroxide, the quaternary bromide forms pyridine and the diphenylmethane derivative; when boiled with glacial acetic acid or acetic anhydride, it yields the diacetate of dibromo-*p*-hydroxymesityl alcohol and dibromo-*p*-acetoxymesityl bromide.

The quaternary *bromide*, $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{C}_9\text{NH}_7\text{Br}$, melts at 266—267°, yields quinoline and the diphenylmethane when treated with cold dilute sodium hydroxide, and when boiled with glacial acetic acid yields the diphenylmethane derivative and dibromo-*p*-acetoxymesityl acetate, or, with acetic anhydride, the same diacetate together with dibromo-*p*-acetoxymesityl bromide.

The aniline derivative, $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{NHPH}$, yields traces of aniline when boiled with glacial acetic acid or dilute sodium hydroxide, and gradually decomposes when heated on the water-bath. The *acetyl* derivative, $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{NPhAc}$, melts at 238° ; the *diacetyl* derivative, $\text{OAc}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{NPhAc}$, melts at $168\text{--}169.5^\circ$.

The *methylamine* derivative from dibromo-4-acetoxymesityl bromide, $\text{NMe}(\text{CH}_2\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{OAc})_2$, crystallises in small, white plates, melts at 218° , and remains unchanged when boiled with glacial acetic acid or acetic anhydride, or when heated on the water-bath. The *diamylamine* derivative, $\text{OAc}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{N}(\text{C}_5\text{H}_{11})_2$, crystallises in large, stout, colourless prisms, melts at 63° , and does not decompose when boiled with glacial acetic acid or acetic anhydride, or when heated on the water-bath. The *diethylamine* derivative, $\text{OAc}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{NEt}_2$, crystallises in glistening, stout rhombohedra, melts at 94° , and remains unchanged when boiled with glacial acetic acid or acetic anhydride.

Dibromo-p-methoxymesityl bromide, $\text{OMe}\cdot\text{C}\begin{smallmatrix} \text{CMe}\cdot\text{CBr} \\ \text{CMe}\cdot\text{CBr} \end{smallmatrix}\text{C}\cdot\text{CH}_2\text{Br}$, is prepared by the action of hydrogen bromide in glacial acetic acid solution on dibromo-*p*-methoxymesityl methyl ether, which is formed when dibromo-*p*-hydroxymesityl alcohol is boiled with methyl iodide and sodium in methyl-alcoholic solution. It crystallises in long, thin needles and melts at 143° . The *methylamine* derivative, $\text{NMe}(\text{CH}_2\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{OMe})_2$, which crystallises in small, white plates and melts at 180° , and the *diamylamine* derivative,



which crystallises in glistening, colourless prisms and melts at 164° , remain unchanged when boiled with glacial acetic acid or acetic anhydride, or when heated on the water-bath. The *pyridine* derivative, $\text{OMe}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_5\text{Br}$, melts at 226° and decomposes into its components when boiled with glacial acetic acid.

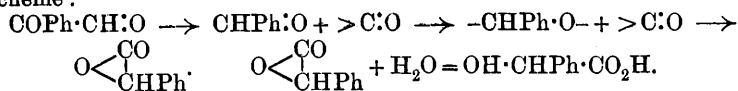
4:6-Dibromo-2-hydroxymesitylpiperidine, $\text{C}_{14}\text{H}_{19}\text{ONBr}_2$, formed from piperidine and dibromo-2-hydroxymesityl bromide, crystallises in glistening, rhombic plates, melts at $91\text{--}92^\circ$, and when boiled with acetic anhydride yields dibromo-2-acetoxymesityl acetate melting at $98\text{--}99^\circ$.

With the exception of the ethyl-, benzyl-, diethyl-, and diamylamine, piperidine, and aniline derivatives of dibromo-*p*-hydroxymesityl bromide, the condensation products described above remain unchanged when heated on the water-bath.

G. Y.

Behaviour of Benzoylcarbinol towards Alkalis and Oxidising Agents. WM. LLOYD EVANS (*Amer. Chem. J.*, 1906, 35, 115—144).—It has been shown by Nef (*Abstr.*, 1905, i, 7) that copper acetate and sulphate are reduced by benzoylcarbinol in aqueous solution at the ordinary temperature to cuprous oxide and metallic copper respectively. The benzoylcarbinol is oxidised in these reactions to benzoylformaldehyde, which, when treated with aqueous sodium hydroxide or when heated with aqueous copper acetate or sulphate, is converted into *r*-mandelic acid. Nef concluded that the formation of *r*-mandelic acid from benzoylformaldehyde is due to a benzilic acid rearrangement, the benzoylformaldehyde being first dissociated into

benzaldehyde and carbon monoxide in accordance with the following scheme :



A study has been made of the behaviour of benzoylcarbinol and benzoylformaldehyde towards oxidising agents under various conditions. For details of the experiments, the original must be consulted. It has been found that benzoylformaldehyde is converted quantitatively into *r*-mandelic acid by soluble alkali hydroxides at the ordinary temperature and by aqueous copper acetate at 70—100°. The following facts support Nef's assumption that, in the formation of *r*-mandelic acid, the benzoylformaldehyde first undergoes dissociation into benzaldehyde and carbon monoxide. When benzoylformaldehyde is treated with freshly precipitated mercuric or silver oxide, it yields benzoic acid and carbon dioxide only; experiments with mandelic and benzoylformic acids have shown that this oxidation cannot involve the intermediate formation of these acids. With cupric oxide and alkali hydroxide, or with potassium ferricyanide and potassium hydroxide, the aldehyde is completely converted into *r*-mandelic acid. When the aldehyde is treated with cold aqueous potassium permanganate, benzoic acid is the sole product, but in presence of alkali hydroxide, benzoylformic, benzoic, and carbonic acids are produced, the benzoylformic acid being due to the oxidation of *r*-mandelic acid formed as an intermediate product. It is shown that these results can only be interpreted in accordance with the scheme suggested by Nef.

When benzoylcarbinol is heated at about 600°, it undergoes decomposition with evolution of gas and formation of benzene and benzaldehyde, whence it is concluded that the compound is dissociated by heat into benzaldehyde and formaldehyde.

If bromoacetophenone is treated with copper sulphate and sodium hydroxide at the ordinary temperature, it is converted into mandelic acid, whilst at 100°, benzoic, mandelic, and benzoylformic [phenylglyoxylic] acids are produced.

By the oxidation of acetophenone with potassium ferricyanide and potassium hydroxide, phenylglyoxylic and benzoic acids are formed, but no trace of mandelic acid is produced; it is evident, therefore, that this reaction does not proceed in a manner analogous to the oxidation of benzoylcarbinol and bromoacetophenone.

When benzoylcarbinol is treated with alkali hydroxide, alcoholic potassium hydroxide, or sodium ethoxide, a dark yellow, non-volatile, resinous product is formed, together with a small quantity of benzoic acid and traces of *trans*-tribenzoylcyclotrimethylene.

Paal and Schulze (Abstr., 1903, i, 707) have assigned the formula $\text{OH}\cdot\text{CPh}\cdot\text{CBr}\cdot\text{CH}\cdot\text{CPh}\cdot\text{OH}$ to their α - and β -bromodiphenacyls. A number of objections are raised to the validity of this formula, and evidence is adduced in favour of the formulæ $\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{Ph}$ and $\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{Ph}$ HCBr , the former representing the α -compound or *cis*- α -

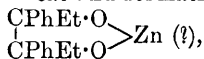
phenacyloxy- ω -bromostyrene, and the latter the β -compound or the *trans*-modification.

When α - and β -bromodiphenacyls are treated with a solution of fused sodium acetate in acetic acid at 100° , 66—68 per cent. of the theoretical quantity of benzoylcarbinyl acetate is produced. The α - and β -acetoxydiphenacyls on similar treatment also give a large yield of benzoylcarbinyl acetate. When α - and β -dibromophenacyl are reduced with zinc dust and alcohol, the chief product of the reaction is a non-volatile *oil*, probably α -phenacyloxystyrene, $\text{CH}_2\text{:CPh}\cdot\text{O}\cdot\text{CH}_2\text{Bz}$, small quantities of diphenacyl and acetophenone being also formed.

If α - or β -bromophenacyl is heated in a sealed tube for six hours at 100° with a solution of potassium formate in methyl alcohol, β -*hydroxydiphenacyl* is obtained, which crystallises from hot benzene in microscopic needles, melts at 175 — 178° , and when heated with fused sodium acetate and glacial acetic acid yields benzoylcarbinyl acetate together with a non-volatile tarry product.

The existence of Paal and Schulze's δ -iodophenacyl (Abstr., 1903, i, 709) is regarded as very doubtful, and it is suggested that it consists merely of the β -isomeride. E. G.

The Pinacone from Phenyl Ethyl Ketone. HEDWIG STERN (*Monatsh.*, 1905, 26, 1559—1567. Compare Barry, this Journal, 1874, 74).—When reduced with sodium and aqueous sodium carbonate, phenyl ethyl ketone yields a mixture of phenylethylcarbinol and the unchanged ketone, boiling at 110 — 180° under 26 mm. pressure, and the *pinacone*, $\text{OH}\cdot\text{CPhEt}\cdot\text{CPhEt}\cdot\text{OH}$, boiling at 210° under the same pressure. The pinacone, which is obtained in a yield of 8 per cent. of the theoretical, crystallises in glistening, white plates, melts at 132° , is readily soluble in alcohol, ether, acetone, toluene, or carbon disulphide, but is insoluble in water, and remains unchanged when heated with 20 per cent. sulphuric acid on the water-bath or at 120° , or when boiled with acetic anhydride and sodium acetate. When oxidised with chromic acid in glacial acetic acid solution, it yields phenyl ethyl ketone boiling at 211° . In toluene solution, the pinacone interacts with zinc ethyl, with development of heat and formation of a *substance*,



which is decomposed by water, forming zinc hydroxide and regenerating the pinacone. When boiled with acetyl chloride, the pinacone yields (a) a small quantity of an oil, which boils at 211° , and is probably a mixture of phenyl ethyl ketone and phenylethylcarbinol, and (b)

an unsaturated *hydrocarbon*, $\begin{array}{c} \text{CPh}\cdot\text{CHMe} \\ | \\ \text{CPh}\cdot\text{CHMe} \end{array}$ or $\begin{array}{c} \text{CPhEt}\cdot\text{CH}_2 \\ | \\ \text{CPh}=\text{CH} \end{array}$, which crystallises in white leaflets resembling mica, melts at 99° , and boils at 158° under 8 mm. pressure. It forms a *dibromide*, $\text{C}_{18}\text{H}_{18}\text{Br}_2$, which is obtained in yellow crystals, decomposes at 90° , and is soluble in carbon disulphide. G. Y.

Constitution of α and β -Benzopinacolins. FRIEDRICH WERTHEIMER (*Monatsh.*, 1905, 26, 1533—1544. Compare Thörner and Zincke, Abstr., 1878, 222, 425, 874; Lieben, Abstr., 1905, i, 167).—The

benzopinacolins are obtained in similar yields by Thörner and Zincke's (*loc. cit.*) and Paal's (Abstr., 1884, 1167) methods of preparation. Of the product obtained by Paal's method, 20—25 per cent. consists of the α -isomeride. Tables are given showing the melting points of mixtures containing varying amounts of the α - and β -isomerides; that containing 27 per cent. of α -benzopinacolin melts at about 158.6° .

The α - and β -benzopinacolins do not form oximes, remain unchanged when heated with water at 190 — 200° , and, contrary to Delacre's statement (*Beilstein*, III, 264), do not interact with zinc ethyl at 130 — 140° . They are not oxidised by potassium permanganate in sulphuric acid solution on the water-bath, and are not reduced by aluminium amalgam and boiling alcohol.

β -Benzopinacolin remains unaltered when treated with zinc dust in glacial acetic solution, whilst the same treatment converts α -benzopinacolin into the mixture of the two isomerides melting at 159° . They do not form acetyl derivatives when heated with acetic anhydride and sodium acetate at 137° . When boiled with alcoholic potassium hydroxide in a reflux apparatus, α -benzopinacolin remains unchanged, whilst the β -isomeride yields triphenylmethane and benzoic acid. γ -Benzopinacolin must be an oxide, but not the $\alpha\beta$ -oxide, and may have the structure $\begin{array}{c} \text{CHPh} \cdot \text{C}_6\text{H}_4 \\ | \\ \text{CPh}_2 - \text{O} \end{array}$; the ease with which α -benzopinacolin is converted into its β -isomeride, and the fact that both yield the same tetranitro-derivative (Biltz, Abstr., 1897, i, 523), show that they must be similarly constituted. G. Y.

Cholesterol. III. OTTO DIELS and EMIL ABDERHALDEN (*Ber.*, 1906, 39, 884—890. Compare Abstr., 1904, i, 880; Windaus and Stein, *ibid.*, 1010).—The authors have studied the question as to the position of the alcohol group in the cholesterol molecule relatively to the double linking. By the action of hydroxylamine on cholestenone, there was formed, in addition to the normal oxime, a second substance, which was probably a compound formed by the addition of hydroxylamine to cholestenone, the addition taking place at the double linking; this behaviour appears to indicate that cholestenone is an $\alpha\beta$ -unsaturated ketone, a view which the authors adduce with reserve.

When cholesterol is reduced by sodium and boiling amyl alcohol, the reduction takes place at the double linking, and the saturated alcohol, α -cholestanol, $\text{C}_{27}\text{H}_{48}\text{O}$, is formed according to the equation $\text{C}_{27}\text{H}_{46}\text{O} + \text{H}_2 = \text{C}_{27}\text{H}_{48}\text{O}$. Cholestenone, when similarly reduced, forms the isomeric β -cholestanol. Those results accord with the supposition that cholesterol and cholestenone are $\alpha\beta$ -unsaturated compounds. α -Cholestanol is entirely different from Bondzýnski and Humnicki's coprosterol. It begins to soften at 117 — 118° and melts completely at 126 — 127° ; when quickly heated, softening also begins at 118° , but the melting is complete at 124 — 125° . α -Cholestanol separates from ethyl alcohol, acetone, or ethyl acetate in prisms or plates. A saturated solution in acetic anhydride gives an indigo-blue coloration with concentrated sulphuric acid. Its *benzoyl* derivative softens at 126° and melts at 128 — 129° . When oxidised in glacial acetic acid solution by chromic acid, α -

cholestanol forms α -cholestanone, $C_{27}H_{46}O$, which crystallises in prisms, softens at about 116° , and melts at 118 — 119° .

β -Cholestanol, $C_{27}H_{48}O$, formed by the reduction of cholestenone by boiling amyl alcohol and sodium, softens at about 140° and melts at 142 — 143° . When oxidised in glacial acetic acid solution by chromic acid, it forms β -cholestanone, $C_{27}H_{46}O$, which melts at 128 — 129° .

A. McK.

Isomorphous Substitution of the Elements Fluorine, Chlorine, Bromine, and Iodine in Organic Molecules. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 8, 613—623).—Methyl *p*-iodobenzoate crystallises in colourless needles melting at 114° and isomorphous with the analogous bromine compound. Crystallographical and physical facts are adduced to prove that the three halogenated esters of *p*-benzoic acid are dimorphous.

E. F. A.

Methyl Amino-*p*-dimethylaminobenzoate. FRÉDÉRIC REVERDIN and ERNEST DELÉTRA (*Ber.*, 1906, 39, 971—974).—The nitration of methyl *p*-dimethylaminobenzoate with nitric acid of sp. gr. 1.34 readily yields a mononitro-derivative, which melts at 71.5° and is reduced by tin and hydrochloric acid to the amino-compound, the hydrochloride of which forms white leaflets and melts at 228° . The acetyl compound, $C_{12}H_{16}O_3N_2$, melts at 232° . The picrate forms yellow crystals and explodes on heating. The base forms a condensation product with chlorodinitrobenzene which melts and decomposes at 253 — 254° . The base is readily diazotised and yields dyes of no practical interest.

Methyl hydroxy-*p*-dimethylaminobenzoate, $C_{10}H_{13}O_3N$, crystallises in long prisms and melts at 176.5° . The barium derivative forms glassy, red leaflets.

C. S.

Sulphobenzoic Acids and their Nitro-derivatives obtained by the Action of Anhydrous Nitric Acid. HERMAN J. TAVERNE (*Rec. trav. chim.*, 1906, 25, 50—74).—*o*-Sulphobenzoic acid crystallises with $3H_2O$ and melts at 70° ; the anhydrous acid melts at 141° (compare Krannich, *Abstr.*, 1901, i, 153).

5-Nitro-2-sulphobenzoic acid is prepared by dissolving *o*-sulphobenzoic acid in excess of anhydrous nitric acid, evaporating the excess of acid at a temperature not exceeding 50° , and exposing the residue under reduced pressure over sulphuric acid. The pure acid (hydrated) regenerated from the recrystallised potassium salt melts at 105° , is soluble in water and alcohol, slightly so in ether, and insoluble in benzene; the anhydrous acid is very hygroscopic and melts at 153° . The constitution of the acid was determined by its conversion into 2-chloro-5-nitrobenzoic acid by the action of phosphorus pentachloride, preliminary trials with sulphobenzoic and nitrosulphobenzoic acids having shown that this reagent could safely be used for this purpose.

m-Sulphobenzoic acid was prepared by hydrolysing ethyl *m*-sulphaminobenzoate with sulphuric acid or by sulphonating benzoic acid (compare Gattermann, *Abstr.*, 1891, 1226). It forms efflorescent crystals with $2H_2O$, melts at 98° , and on exposure in a vacuum desiccator slowly becomes anhydrous and then melts at 141° . When nitrated by the method already described, it yields 2-nitro-3-sulpho-

benzoic acid, which may be identical with that prepared by Limpricht and Uslar (*Annalen*, 1858, 106, 27). It crystallises with H_2O , melts at 96° , becomes anhydrous when dried in a vacuum desiccator over sulphuric acid, and then melts at 159.5° . The constitution of the acid was determined by its conversion into 2:3-dichlorobenzoic acid (Seelig, *Abstr.*, 1887, 362) by the action of phosphorus pentachloride.

p-Sulphobenzoic acid was prepared either from *p*-sulphaminobenzoic acid or by the oxidation of toluene-*p*-sulphonic acid. It forms efflorescent crystals with $3\text{H}_2\text{O}$, melts at 94° , slowly becomes anhydrous when exposed in a vacuum desiccator over sulphuric acid, and then melts at $259\text{--}260^\circ$. When nitrated with anhydrous nitric acid or with a mixture of nitric and sulphuric acids, it yields 3-nitro-4-sulphobenzoic acid, which crystallises with $2\text{H}_2\text{O}$ and melts at $125\text{--}126^\circ$; the anhydrous acid melts at 159° (compare Hart, *Abstr.*, 1881, 1144). When treated with phosphorus pentachloride, this yields a mixture of 3-nitro-4-chlorobenzoic (m. p. 179°) and 3:4-dichlorobenzoic acids (m. p. 201°).

The analogies observed between the results of the nitration of the chlorobenzoic acids (Montagne, *Abstr.*, 1900, i, 491) and the sulphobenzoic acids, and the changes in melting points of the members of the two series of acids resulting from the introduction of a nitro-group are discussed in the original.

T. A. H.

Stereochemistry of the Cinnamic Acids. EMIL ERLENMEYER, jun. (*Ber.*, 1906, 39, 788—791. Compare Erlenmeyer, *Abstr.*, 1883, 196; 1891, 1482; 1896, i, 302).—*r*- α -Bromo- β -phenyl- β -lactic acid is resolved into its active components by means of cinchonine, the salt of the *d*-acid crystallising out first, or by means of strychnine; the *d*-acid melts at 118° and has $[\alpha]_D + 22.6^\circ$.

r- α -Chloro- β -phenyl- β -lactic acid and *r*-dibromohydrocinnamic acid are resolved by means of strychnine. *d*- α -Chloro- β -phenyl- β -lactic acid melts at 116° and has $[\alpha]_D + 26.11^\circ$. *l*-Dibromohydrocinnamic acid has $[\alpha]_D - 68.3^\circ$, and when boiled with water yields *d*- α -bromo- β -phenyl- β -lactic acid.

r- α -Iodo- β -phenyl- β -lactic acid is resolved by means of cinchonine; the *d* acid melts at 122° and has $[\alpha]_D + 17^\circ$.

Sodium *l*-oxyphenylacrylic acid, having $[\alpha]_D - 157.89^\circ$, is obtained by the action of aqueous sodium hydroxide on *d*- α -chloro- and on *d*- α -iodo- β -phenyl- β -lactic acids, and when treated with hydrogen chloride yields *d*- β -chloro- β -phenyl- α -lactic acid, melting at 144° and having $[\alpha]_D - 71.7^\circ$.

d- β -Phenyl- β -lactic acid, formed by reduction of *d*- α -bromo- β -phenyl- β -lactic acid, melts at 116° and has $[\alpha]_D + 19^\circ$.

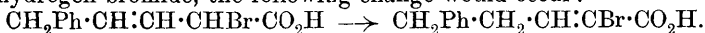
The oily by-product obtained in Erlenmeyer and Lipp's preparation of chlorophenyl-lactic acid (*Abstr.*, 1883, 992), when resolved by means of strychnine, yields two chlorophenyl-lactic acids, having $[\alpha]_D - 16.62^\circ$ and 13.76° respectively.

G. Y.

Cinnamylideneacetic Acid [Styrylacrylic Acid] and some of its Transformation Products. ARTHUR MICHAEL and WIGHTMAN W. GARNER (*Amer. Chem. J.*, 1906, 35, 258—267).—An improved method is described for the preparation of $\alpha\beta$ -dibromo- δ -phenyl-

pentenoic acid. When this acid (1 mol.) is treated with alcoholic potassium hydroxide (2 mols.), a product is obtained consisting of at least two bromo- δ -phenylpentenoic acids, which do not appear to be stereoisomerides, as the melting point ($67-75^\circ$) of the mixture remains unchanged after repeated fusion. When the mixture is converted into the ethyl ester and the latter is boiled with alcoholic potassium hydroxide, a propiolic derivative is not obtained, but styrylacrylic acid is produced. *Ethyl δ -phenyl- Δ^{β} -pentenoate* was obtained as an oil boiling at 178° under 25 mm. pressure, and was converted into the dibromo-derivative by the action of a solution of bromine in carbon disulphide. On treating this substance with alcoholic potassium hydroxide, an uncrystallisable product was obtained which was converted into the ethyl ester, which boiled at $178-184^\circ$ under 8-11 mm. pressure, but suffered decomposition, and was therefore unsuitable for further experiments.

Fittig (Abstr., 1895, i, 204) has shown that when Δ^{β} -unsaturated acids which contain an alkyl or a benzyl group are boiled with alkali hydroxide, they are mainly converted into the Δ^{α} -isomerides, but that the latter are partly changed into β -hydroxy-acids, which undergo partial conversion into the original Δ^{β} -acids. If, however, the alkyl or benzyl group is replaced by phenyl, only traces of the acid undergo such a rearrangement. If this intramolecular rearrangement in bromo- δ -phenyl- Δ^{β} -pentenoic acid precedes the elimination of hydrogen bromide, the following change would occur:



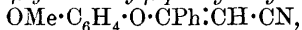
In order to obtain evidence on this point, a number of aromatic acids were oxidised with potassium permanganate under different conditions. It was found that acids of the cinnamic acid type, such as cinnamic, α -bromocinnamic, α -ethyleinnamic, and α -butyleinnamic acids invariably yield benzaldehyde when oxidised in presence of dilute sodium carbonate or strong potassium hydroxide. Phenylacetic acid gives benzaldehyde when dissolved in dilute sodium carbonate, but does not yield the aldehyde in presence of strong potassium hydroxide. β -Phenylpropionic acid does not furnish benzaldehyde either in presence of sodium carbonate or alkali hydroxide. δ -Phenyl- Δ^{α} -pentenoic acid gives the aldehyde in presence of alkali hydroxide, but the aldehyde is not formed by the oxidation of the free acid. The difference in the behaviour of β -phenylpropionic acid and δ -phenyl- Δ^{α} -pentenoic acid is probably due to the action of the alkali hydroxide on the latter, converting it partially into the Δ^{β} -acid, which yields benzaldehyde on oxidation. The mixture of bromo-acids produced by the action of alcoholic potassium hydroxide on $\alpha\beta$ -dibromo- δ -phenylpentenoic acid yields benzaldehyde when oxidised in the free state, and also in presence of sodium carbonate or potassium hydroxide. It is suggested, therefore, that at least a part of the mixture of bromo-acids is converted into an acid in which the double linking is nearer to the phenyl than it is in a Δ^{α} -acid, and that the production of styrylacrylic acid takes place without the intermediate formation of a propiolic derivative.

β -Phenylpropaldehyde semicarbazone crystallises in colourless leaflets and melts at 125° .

E. G.

Condensation of Acetylenic Nitriles with Phenols. General Method of Synthesis of β -Substituted β -Phenoxyacrylonitriles.

CHARLES MOUREU and I. LAZENNEC (*Compt. rend.*, 1906, 142, 450—451. Compare this vol., i, 148; Moureu, *Abstr.*, 1903, i, 698; 1904, i, 286; Moureu and Brachin, *Abstr.*, 1904, i, 811; Ruhemann and Beddow, *Trans.*, 1900, 77, 984, 1119; Ruhemann and Stapleton, *ibid.*, 1179).—The β -substituted β -phenoxyacrylonitriles are readily prepared by heating at 120—140° a mixture of the sodium derivative of the phenol and the acetylenic nitrile. β -Phenoxy- β -amylacrylonitrile, $C_5H_{11}\cdot C(OPh):CH\cdot CN$, boils at 175—178° under 15 mm. pressure; *o*-tolyl-oxy- β -hexyl- β -acrylonitrile, $C_6H_{13}\cdot C(O\cdot C_6H_4Me):CH\cdot CN$, boils at 195—196° under 15 mm. pressure; β -phenoxy- β -phenylacrylonitrile, $OPh\cdot CPh:CH\cdot CN$, melts at 85—86°; *o*-tolyl-oxy- β -phenyl- β -acrylonitrile, $C_6H_4Me\cdot O\cdot CPh:CH\cdot CN$, melts at 104—105°; β -thymoxy- β -phenylacrylonitrile, $C_6H_3MePr^{\beta}\cdot O\cdot CPh:CH\cdot CN$, boils at 226—229° under 11 mm. pressure, and β -guaiacoxy- β -phenylacrylonitrile,



melts at 90—91°. These compounds are hydrolysed by alcoholic potassium hydroxide to form the corresponding ketone and phenol, thus β -phenoxy- β -phenylacrylonitrile yields acetophenone and phenol.

M. A. W.

Coumarins from *m*-Cresol. K. FRIES and W. KLOSTERMANN (*Ber.*, 1906, 39, 871—875).—Whilst the formation of coumarins from phenol, *o*-cresol, or *p*-cresol and malic acid or ethyl acetoacetate respectively proceeds with difficulty according to Pechmann's method, it takes place readily with *m*-cresol.

7-Methylcoumarin, $\begin{array}{c} CMe\cdot CH:C\cdot O\cdot CO \\ | \\ CH\cdot CH:C\cdot CH:CH \end{array}$, prepared by the addition

of sulphuric acid to a mixture of *m*-cresol and malic acid, separates from dilute alcohol in needles and melts at 128°. The authors' observations with this substance are at variance with those of Schmidt (*Inaug. Diss.*, Rostock, 1897), who prepared it by the Perkin synthesis from sodium acetate and *m*-homosalicylaldehyde. Chuit and Bolsing (this vol., i, 185) give 126° as the melting point. When fused with sodium hydroxide, 7-methylcoumarin forms 4-methylsalicylic acid, melting at 177°. When boiled for several hours with sodium ethoxide, 7-methylcoumarin forms ethyl 4-methylcoumarate, melting at 105°, from which 4-methylcoumaric acid is formed on saponification; the latter separates from alcohol in needles and decomposes at 195°.

4:7-Dimethylcoumarin, $C_9H_8O_2Me_2$, prepared by the action of sulphuric acid on a mixture of *m*-cresol and ethyl acetoacetate, separates from alcohol in needles and melts at 132°. When fused with sodium hydroxide, it forms 4-methylsalicylic acid. When boiled for five hours with 33 per cent. aqueous potassium hydroxide, it is converted into β -4-dimethylcoumaric acid, which separates from water in needles and melts and decomposes at 142°. When boiled with sodium ethoxide, it does not form coumaric acid, but is converted into the compound, $C_{21}H_{22}O_3$, which contains a phenolic group and is presumably bisdimethylhydrocoumarone ketone.

3:4:7-Trimethylcoumarin, prepared by the action of sulphuric acid

on a mixture of *m*-cresol and methyl ethylacetoacetate, separates from alcohol in glistening needles and melts at 114°. It is not decomposed when boiled with aqueous potassium hydroxide or with sodium ethoxide.

A. McK.

Chlorination of Indigotin. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 163280).—It is not possible to chlorinate indigotin by the methods employed for bromination, as decomposition then occurs. Indigo-white and its homologues may be chlorinated in strong hydrochloric acid solution, the temperature not being allowed to rise above 20°. To prepare a monochloro-derivative, 2 mols. of chlorine are required, 1 mol. being necessary to oxidise the indigo-white to indigotin. The intermediate formation of a chloroindigo-white may be recognised, but the isolation of this compound is not practicable.

Chloroindigotin forms a blue powder, dissolving more readily in organic solvents than indigotin. It sublimes and partially decomposes on heating, and is reduced by alkali hyposulphites. By the employment of larger quantities of chlorine, higher chlorinated products may be prepared.

C. H. D.

New Syntheses of Derivatives of Fluorene and of Diphenyl. GIORGIO ERRERA and G. LA SPADA (*Gazzetta*, 1905, 35, ii, 539—553).

—3-Hydroxyfluorenone-2-carboxylic acid, $\begin{array}{ccccccc} \text{CH}:\text{CH}:\text{C}:\text{CO}:\text{C}:\text{CH}:\text{C}:\text{CO}_2\text{H} \\ | & & | & & | & & | \\ \text{CH}:\text{CH}:\text{C} & \text{---} & \text{C}:\text{CH}:\text{C}:\text{OH} \end{array}$,

prepared by the action of 25 per cent. potassium hydroxide solution on ethyl indandionemethenylacetoacetate, separates in yellow needles, melts and decomposes at 277—279°, and is soluble in acetic acid or xylene and, to a slight extent, in water, alcohol, or light petroleum. It acts as a dibasic acid. The *potassium*, *sodium* (+ 2H₂O), and *silver* salts were prepared. The *methyl* ester, C₁₅H₁₀O₄, crystallises from xylene in yellow needles melting at 250° and dissolves slightly in methyl or ethyl alcohol or light petroleum, and readily in dilute solutions of the alkali hydroxides.

Methyl 3-methoxyfluorenone-2-carboxylate, OMe·C₁₃H₆O·CO₂Me, prepared from the corresponding hydroxy-ester by the action of potassium hydroxide solution and methyl sulphate, crystallises from light petroleum in yellow needles melting at 169° and is slightly soluble in methyl alcohol. The corresponding *acid*, C₁₅H₁₀O₄, crystallises from acetic acid in minute, yellow needles melting and decomposing at 261° and dissolves sparingly in methyl or ethyl alcohol or light petroleum and, in larger amount, in solutions of the alkali hydroxides or carbonates, yielding orange-red liquids.

3-Hydroxyfluorenone, C₁₃H₇O·OH, prepared by maintaining 3-hydroxyfluorenone-2-carboxylic acid for some time at its melting point, crystallises from xylene in minute, yellow needles melting at 228—229°, and dissolves sparingly in light petroleum and readily in alcohol; it is dissolved by concentrated sulphuric acid, giving a violet liquid, and by alkali hydroxide or carbonates, yielding orange-red solutions. Its *benzoyl* derivative, C₁₃H₇O·OBz, crystallises from aqueous alcohol in shining, golden-yellow plates melting at 150°. The *acetyl* derivative, C₁₃H₇O·OAc, crystallises from alcohol in yellow needles melting at

115°. The *oxime*, $C_{13}H_8O \cdot NOH$, separates from light petroleum as a brown, crystalline powder melting and decomposing at 187—188°, and dissolves sparingly in water, readily in alcohol or acetic acid, and in solutions of bases giving intense orange colorations. The corresponding *methoxy*-compound, $C_{13}H_7O \cdot OMe$, separates from light petroleum in yellow, crystalline incrustations melting at 96—97° and is readily soluble in alcohol.

3-Hydroxydiphenyl-6-carboxylic acid, $OH \cdot C_{12}H_8 \cdot CO_2H$, prepared by the action of potassium hydroxide on the potassium derivative of 3-hydroxyfluorenone, crystallises from water in needles which contain H_2O and melt in their water of crystallisation at 123°; the anhydrous acid melts at 147°. It dissolves in alcohol or light petroleum. The acid dissolves in cold concentrated sulphuric acid, giving a colourless liquid which rapidly becomes violet and, on dilution with water, deposits 3-hydroxyfluorenone. The *sodium*, *potassium*, *silver*, and *calcium* ($+ 3H_2O$) salts are described.

3-Hydroxydiphenyl, $C_{12}H_9 \cdot OH$, prepared by the dry distillation of a mixture of calcium 3-hydroxydiphenyl-6-carboxylate and slaked lime, crystallises from light petroleum in shining, white needles melting at 75° and boils above 300°; it dissolves in cold alkali hydroxide solutions, in hot alkali carbonate solutions, in water sparingly, and in alcohol or light petroleum more readily. The *benzoyl* derivative, $C_{12}H_9 \cdot OBz$, crystallises from alcohol in silvery plates melting at 60—61°.

T. H. P.

Butadiene Compounds. XV. Colour of Methoxy-derivatives of Mono-, Di-, and Tri-phenylfulgides. HANS STOBBE (*Ber.*, 1906, 39, 761—769. Compare *Abstr.*, 1904, i, 589, 672; this vol., i, 22, 91, 183).—The following table gives the colours of the fulgides and the wave-lengths of the spectrum; the first number denotes the beginning of the visible absorption, the following number the commencement of total absorption in $N/32$ solution in chloroform:

α -p-Methoxyphenyl- $\delta\delta$ -dimethylfulgide	Yellow	446	436
δ -Phenyl- α -p-methoxyphenylfulgide	Orange	494	479
$\delta\delta$ -Diphenyl- α -p-methoxyphenylfulgide	Orange-red	539	521
α -o-Methoxyphenyl- $\delta\delta$ -dimethylfulgide	Yellow	443	428
$\delta\delta$ -Diphenyl- α -o-methoxyphenylfulgide	Dark red	534	527
α -Phenyl- $\delta\delta$ -dimethylfulgide	White or light yellow	418	412
$\alpha\delta$ -Diphenylfulgide	Citron-yellow	456	448
$\alpha\delta\delta$ -Triphenylfulgide	Orange-red	537	513

The colour of the fulgides is not influenced by replacing the methoxy- by the ethoxy-group.

[With ALFRED LENZNER.]— α -p-Methoxyphenyl- $\delta\delta$ -dimethylfulgenic acid, $OMe \cdot C_6H_4 \cdot CH : C(CO_2H) \cdot C(CO_2H) : CMe_2$, from anisaldehyde and ethyl dimethylitaconate, forms small, white crystals and melts, decomposes, and turns yellow at 226—227°. The *fulgide*, $C_{15}H_{14}O_4$, melts at 114.5°.

α -o-Methoxyphenyl- $\delta\delta$ -dimethylfulgenic acid, $C_{15}H_{16}O_5$, from o-methoxybenzaldehyde and ethyl dimethylitaconate, melts and decomposes at

200°. The *fulgide*, $C_{15}H_{14}O_4$, melts at 97.5° and separates from carbon disulphide in glassy, yellow crystals which contain carbon disulphide and effloresce rapidly in the air.

[With KARL KAUTZSCH and TH. BADENHAUSEN.]—*δ-Phenyl-α-p-methoxyphenylfulgenic acid* is obtained from anisaldehyde and diethylphenylitaconate and is white. The *fulgide*, $C_{19}H_{14}O_4$, melts at 144—147°.

[With RUDOLF NETTEL.]—*δδ-Diphenyl-α-p-methoxyphenylfulgenic acid*, $C_{25}H_{20}O_5$, from anisaldehyde and ethyl diphenylitaconate, separates from chloroform or benzene in white crystals containing 1 mol. of the solvent, the former compound melting and decomposing at 211°. The *sodium* and *barium* salts are described. The *fulgide*, $C_{25}H_{18}O_4$, melts at 194°.

α-o-Ethoxytriphenylfulgenic acid, $C_{26}H_{22}O_5$, from *o*-ethoxybenzaldehyde and ethyl diphenylitaconate, forms yellow crystals containing C_2H_6O . The *sodium* salt is described. The *fulgide*, $C_{26}H_{20}O_4$, melts at 181°, is stable towards water, and yields salts of the fulgenic acid by treatment with alkalis or piperidine.

[With ERICH BENARY.]—*δδ-Diphenyl-α-o-methoxyphenylfulgenic acid*, $C_{25}H_{20}O_5$, from *o*-methoxybenzaldehyde and ethyl diphenylitaconate, turns red at 205°, melts and decomposes at 229—231°, and separates from alcohol in yellow prisms which contain C_2H_6O and slowly effloresce in the air. The *sodium* salt is described. The *fulgide*, $C_{25}H_{18}O_4$, softens and melts at 200°. C. S.

Butadiene Derivatives. XVI. Anomalies in the Synthesis of Fulgenic Acids. HANS STOBBE and TH. BADENHAUSEN (*Ber.*, 1906, 39, 769—772).—When benzaldehyde is condensed with ethyl $\gamma\gamma$ -diphenylitaconate in alcoholic solution containing sodium ethoxide, $\alpha\delta\delta$ -triphenylfulgenic acid is obtained (*Abstr.*, 1904, i, 672), but on attempting to prepare the latter acid by the interaction of benzophenone, ethyl phenylitaconate, and sodium ethoxide in ethereal solution, a lactonic acid, which is either γ -diphenyl- α -benzylidenepara-

conic acid, $CHPh:C\begin{smallmatrix} \text{CO} & \text{---} & \text{O} \\ & \diagdown & / \\ & \text{CH}(\text{CO}_2\text{H}) \end{smallmatrix} > CPh_2$, or γ -phenyl- α -diphenyl-

methyleneparaconic acid, $CPh_2:C\begin{smallmatrix} \text{CO} & \text{---} & \text{O} \\ & \diagdown & / \\ & \text{CH}(\text{CO}_2\text{H}) \end{smallmatrix} > CHPh$, is produced.

It crystallises from chloroform or 60 per cent. acetic acid in white needles, melts at 203—205°, gives benzophenone on oxidation with potassium permanganate, and is converted into $\alpha\delta\delta$ -triphenylfulgenic acid by boiling for two hours with alcoholic sodium hydroxide or ethoxide. $\alpha\delta\delta$ -Triphenylfulgenic acid, however, cannot be converted into the lactonic acid by heating it with acetic anhydride containing a few drops of sulphuric acid.

The production of a lactonic acid under the conditions stated shows that the fulgenic acid syntheses probably take place through the intermediate formation of a derivative of paraconic acid as in the normal Fittig syntheses. In most cases, the paraconic acid is converted into the corresponding fulgenic acid by the action of the sodium ethoxide used in the syntheses. W. A. D.

Lichens and their Characteristic Constituents. X. OSWALD HESSE (*J. pr. Chem.*, 1906, [ii], 73, 113—176).—The author claims priority for the name chrysocetraric acid for the acid $C_{19}H_{16}O_6$ (Abstr., 1895, i, 299). Zopf's pinastric acid (Abstr., 1895, i, 297; 1905, i, 212) was not a pure substance.

The formula $C_{28}H_{22}O_7$, but not Zopf's formula ($C_{13}H_{10}O_3$), for rhizocarpic acid is in agreement with the conversion of the acid into nor-rhizocarpic acid (Abstr., 1899, i, 384), or, when heated with an excess of baryta in a sealed tube at 120° , into alcohol, carbon dioxide, and phenylacetic acid.

Usnea longissima, from Amani, in German East Africa, contains ramalic, *d*-usnic, and dirhizonic acids.

Dirhizonic acid, $C_{18}H_{16}O_5(OMe)_2$, crystallises in small, white needles, melts and decomposes at 189° , is readily soluble in ether, alcohol, acetone, or glacial acetic acid, and dissolves in dilute alkali hydroxides; the alcoholic solution is optically inactive and gives a blue coloration with ferric chloride, but not with bleaching powder. On prolonged boiling with aqueous baryta, the acid yields betorcinol methyl ether and carbon dioxide; the residue from the methoxyl determination contains betorcinol. The *potassium* ($2H_2O$), *sodium* ($2H_2O$), *barium* ($2H_2O$), *calcium* ($3H_2O$), and *copper* salts are described.

The substance observed previously in *Usnea barbata* var. *hirta*, and termed usnarin, is now found to be identical with atranorin. A specimen of this lichen from the island of St. Thomas, in the Gulf of Guinea, contained *d*-usnic and usnaric acids and *santhomic acid*, $C_{11}H_{14}O_4$, which crystallises in colourless, glistening prisms or delicate, white needles, melts and decomposes at 166° , is moderately soluble in water, and in alcoholic solution gives with ferric chloride a bluish-black, with bleaching-powder a bluish-violet, coloration.

A specimen of *Usnea barbata* var. *hirta*, from the east coast of Madras, contained *d*-usnic, usnaric, usnarinic, barbatic, and hirtaic acids.

Usnarinic acid, $C_9H_{10}O_4$, forms a colourless or slightly yellow, granular powder, assumes a brown colour at 200° , decomposes and chars at 240° , has a bitter after-taste, is readily soluble in hot alcohol or glacial acetic acid, and with ferric chloride gives a dark brownish-red coloration; on addition of a drop of moderately-concentrated potassium hydroxide, the acid becomes yellow, changes to red, dissolves in water, and on acidification yields a red, flocculent precipitate; with concentrated sulphuric acid, usnarinic acid gives a yellow coloration changing to red. The *ammonium*, *potassium*, and *sodium* salts are gelatinous.

Hirtaic acid, $C_{15}H_{21}O_5 \cdot OMe$, crystallises in small, colourless, rhombic leaflets, sinters at 130° , melts at 136 — 137° , is readily soluble in ether, alcohol, acetone, glacial acetic acid, or concentrated aqueous potassium hydroxide, carbonate, or hydrogen carbonate, and gives a brownish-red coloration with ferric chloride. The *potassium*, *barium*, *calcium*, and *silver* salts are gelatinous. With concentrated sulphuric acid, hirtaic acid gives a yellow coloration, becoming red on warming; when heated with concentrated nitric acid, it forms a yellow nitro-derivative, and when boiled with hydriodic acid yields methyl iodide and *norhirtaic acid*.

Usnea barbata var. *florida*, from cinchona bark from the east coast

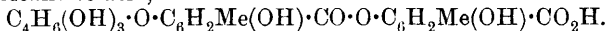
of Madras, contains barbatic acid together with traces of usnaric and *d*-usnic acids.

Alectoria implexa, obtained from the Tarnovaner Wald, near Görz, contains atranorin and an acid which crystallises in small nodules, melts and decomposes at about 178°, and is not alectoric acid.

Contrary to Zopf's statement (Abstr., 1904, i, 1020), *Cornicularia aculeata* contains rangiformic acid.

Roccella phycopsis, from Paximadi Island (Crete), contains erythrin, oxyroccellic and oxalic acids, and *i*-erythritol.

Erythrin, the chromogen of *Roccella montagnei*, *R. fuciformis*, *R. peruensis*, and *R. phycopsis*, is the ester of erythritol and lecanoric acid. Erythric acid, the chromogen of *Aspicilia calcarea farinosa*, is erythrolecanoric acid,



Roccella peruensis (*R. frutectosa*; *R. cacticola*) has been re-examined and found to contain erythrin, erythritol, and oxalic acid.

Cetraria islandica, from the Cavalljoch in the Vorarlberg, contains proto- α -lichesteric acid. The same lichen from the Stubaital, in the Tyrol, contains protolichesteric and proto- α -lichesteric acids. When these acids are dissolved in dilute potassium hydroxide and a current of carbon dioxide passed through the solution, proto- α -lichesteric acid is precipitated first.

The comparison of triethylprotocetraric acid with cetraric acid has been repeated, and the identity of the two acids confirmed (see Abstr., 1905, i, 139). When heated with 97 per cent. alcohol containing a couple of drops of sulphuric acid in a sealed tube at 100°, cetraric acid yields carbon dioxide and triethylcetrul, which forms a blue solution in alcohol and separates as a greenish-blue, amorphous precipitate on dilution with water.

Parmelia tinctorum, from the Regenwald in Amani, German East Africa, contains atranorin and 2½ per cent. of lecanoric acid.

Contrary to Zopf's statement (Abstr., 1905, i, 790), *conspersa* acid from *P. conspersa* is not identical with salazinic acid.

Ochrolechia pallescens (γ) *parella*, from Orcival, in Auvergne, contains parellic and ochrolechiasic acids in the proportion 1:7 or 8. Ochrolechiasic acid, $\text{C}_{22}\text{H}_{14}\text{O}_9$, melts at 282° and does not contain a methoxyl group; the barium and calcium salts crystallise in small needles; the potassium salt forms colourless needles. The acid is precipitated unchanged on acidification of its freshly-prepared solution in dilute potassium hydroxide, but after some minutes it is converted into ochric acid, which crystallises in concentric aggregates of stout prisms, melts and evolves carbon dioxide at 230°, and gives a violet coloration with ferric chloride or a yellow coloration with bleaching powder, and when warmed with concentrated sulphuric acid becomes yellow and finally dark brown.

Sterile *Pertusaria lactea*, from Orcival, in Auvergne, contains lecanoric acid, ochrolechiasic acid, which may be identical with Zopf's violaric acid (Abstr., 1905, i, 212), traces of parellic acid, paric acid, and an acid which melts at 286° and resembles ochrolechiasic acid.

Hämatomma coccineum var. ?, from a wall near Wildbad, contains coccic acid, atranorin, zeorin melting at 236° (m. p. 247—252°; Zopf,

Abstr., 1896, i, 104), and *hydrohämatommin*, $C_{10}H_{18}O$, which crystallises in delicate, white needles, melts at 101° , is tasteless, dissolves readily in alcohol, ether, chloroform, or glacial acetic acid, is neutral, gives with concentrated sulphuric acid a red coloration, becoming blackish-brown when warmed, and when shaken with chloroform and sulphuric acid colours the acid brown, the chloroform red.

Atranorin is a condensation product of betoreinol methyl ester with hämatommic acid, $CO_2Me \cdot C_8H_8O_2 \cdot CO \cdot C_8H_9O_3$. Contrary to the statement of Zopf (Abstr., 1905, i, 212), *Pulveraria chlorina* [*Lepraria* (*Leprea*) *chlorina*] contains small amounts of lepraric acid. It does not give a coloration with alcoholic potassium hydroxide. *L. xanthina*, a sterile, yellow lichen, obtained from Gampertonatal in the Vorarlberg, contains physcion and gives a red coloration with potassium hydroxide.

L. latebrarum, obtained from the porphyrite cliff behind the old castle in Baden-Baden, contains atranorin, an indifferent substance crystallising in needles, leprariac and oxyroccellic acids, and *neobraric acid*, which melts at a few degrees higher than oxyroccellic acid.

The action of dilute potassium hydroxide on parellic acid, $CO_2Me \cdot C_{17}H_{11}O_3(CO_2H)_2$, leads to the formation of *paric acid*, $CO_2Me \cdot C_{13}H_{10}O_4 \cdot CO_2H$, which crystallises in stout, colourless prisms, melts and decomposes at about 230° , gives with ferric chloride an intense blue, with bleaching powder a yellow coloration, and when boiled with aqueous baryta yields carbon dioxide and *parinic acid*, $C_{13}H_{11}O_4 \cdot CO_2H$. This crystallises in delicate glistening needles containing H_2O , commences to become brown at 215° , decomposes at 225° , reddens litmus in alcoholic solution, and dissolves in concentrated sulphuric acid, forming a yellow solution which becomes deep yellow. The *ammonium* salt forms small needles; the *barium* salt, $(C_{14}H_{11}O_6)_2Ba \cdot 4H_2O$, crystallises in small, yellow needles. G. Y.

Two Homosalicylaldehydes derived from *m*-Cresol. PH. CHUIT and FR. BOLSING (*Bull. Soc. chim.*, 1906, [iii], 35, 129—143).—Tiemann and Schotten's supposed *m*-homosalicylaldehyde (Abstr., 1878, 875) has been found by the authors to consist of a mixture of two homosalicylaldehydes, which may be separated by recrystallisation of the mixed oximes from benzene or carbon disulphide, or by fractional distillation with steam from an aqueous solution of sodium carbonate, or by fractional crystallisation of the calcium or barium derivatives of the aldehydes from warm water.

α -m-Homosalicylaldehyde [$Me : OH : COH = 1 : 3 : 4$] crystallises in flattened, colourless needles from alcohol, has an odour recalling that of salicylaldehyde, melts at $59-59.8^{\circ}$, boils at 220.8° under 726 mm. pressure, and is slightly soluble in cold alcohol or warm water. It gives a violet coloration with ferric chloride and yellow with alkalis; the *sodium hydrogen sulphite* compound is crystalline and is decomposed by warm water. The *sodium*, *potassium*, *calcium*, and *barium* derivatives were prepared. The *oxime* crystallises from 50 per cent. alcohol in colourless spangles, melts at $108.5-109^{\circ}$, and is readily soluble in alcohol or benzene, and nearly insoluble in light petroleum.

The *phenylhydrazone* forms colourless, pearly spangles from alcohol and melts at 160—160·5°. The *semicarbazone* crystallises from alcohol, in which it is sparingly soluble, in colourless spangles, which assume a rose tint on exposure to light, melt at 254°, becoming solid and re-melting at 272°.

The *methyl ether* is best prepared by the action of methyl iodide (methylation is incomplete when methyl sulphate is used); it forms colourless needles, melts at 42—43°, boils at 263—264° under 720 mm. pressure, has a feeble odour in the cold, and gives no coloration with ferric chloride; its *oxime* melts at 122·8—123·5°. When fused with potassium hydroxide, the ether undergoes demethylation, yielding *a-m-homosalicylic acid*. When oxidised with potassium permanganate, it furnishes 3-methoxyterephthalic acid. The dimethyl ester of the latter melts at 71·5°, not 65°, as given by Baeyer and Tutein (Abstr., 1889, 1180).

β-m-Homosalicylaldehyde [Me : OH : COH = 1 : 3 : 2] crystallises in long, colourless needles from water, melts at 31·4—31·9°, boils at 228·6° under 728 mm. pressure, and is readily soluble in benzene, slightly so in ether. It gives a violet coloration with ferric chloride, yellow with alkalis, and forms with sodium hydrogen sulphite a solid *additive product*, which is decomposed by hot water. The *sodium*, *potassium*, *calcium*, and *barium* derivatives are crystalline. The *oxime* melts at 111—112° and is readily soluble in alcohol; the *phenylhydrazone* forms bright yellow spangles and melts at 170·2° to 171·4°, and the *semicarbazone* colourless leaflets melting at 214° and re-melting at 244°.

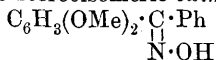
The *methyl ether* crystallises from light petroleum in colourless leaflets, which become yellow on exposure to light, and melts at 41·5—42°. It gives no coloration with ferric chloride. The *oxime* separates from water in colourless needles and melts at 118·5—119·5°. On oxidation with permanganate, the methyl ether yields 3-methoxy-*o-toluic acid* [Me : CO₂H : OMe = 1 : 2 : 3]. This crystallises from water in colourless, flattened needles, melts at 139°, and gives no coloration with ferric chloride. The *methyl ester* is liquid. T. A. H.

cycloHexylacetone. PAUL FREUNDLER (*Compt. rend.*, 1906, 142, 343—345. Compare Abstr., 1905, i, 890).—Magnesium hexahydrobenzyl iodide condenses with acetaldehyde to form *α-cyclohexyl-β-propyl alcohol*, which, on oxidation, yields *cyclohexylacetone* (Bouveault, Abstr., 1904, i, 61). *Hexahydrobenzyl iodide*, C₆H₁₁·CH₂I, prepared by the action of phosphorus tri-iodide or red phosphorus and iodine on the corresponding alcohol, boils at 97—99° under 18—19 mm. pressure. *α-cycloHexylisopropyl alcohol*, C₆H₁₁·CH₂·CHMe(OH), is a liquid with an agreeable odour, boiling at 201—202° under normal pressure and sparingly soluble in water. *cycloHexylacetone*, C₆H₁₁·CH₂·COMe, boils at 197° and has an odour similar to that of camphor; the *hydrogen sulphite* is sparingly soluble and the *semicarbazone* melts at 182·5°. M. A. W.

Fluorogen Groups. A Contribution to the Theory of Partial Valencies. HUGO KAUFFMANN (*Annalen*, 1906, 344, 30—77. Compare Abstr., 1905, i, 280; Kauffmann and Beisswenger,

ibid.).—Fluorescent substances contain two groups of different functions, one of which is the cause of fluorescence and has been termed the fluorogen; the name “luminophore” is now proposed for the other group, which is the source of luminescence. In aromatic compounds, the luminophore is the benzene ring, the activity of which varies with the nature and number of the substituting groups present, being greatest for *p*-diaminobenzene and dimethylaniline, and moderate for aniline and quinol and its ethers. Luminescence is produced by the action of radium rays or of Tesla rays (compare Kauffmann, Abstr., 1904, ii, 691). Tables are given of the comparative results obtained with derivatives of *p*-dimethoxybenzene, by determining the distance at which 5 mg. of radium bromide cause luminescence with and without the intervention of a sheet of zinc. Those derivatives of *p*-dimethoxybenzene which are fluorescent contain as substituting group the unsaturated carbonyl, carboxyl, or cyanogen group, or a group containing an ethylene linking. These fluorogens are also chromophores, but fluorescence is not caused always by the presence of a chromophoric group, probably because strong chromophores interfere, with the luminophoric activity of the benzene ring; thus, highly coloured derivatives of *p*-dimethoxybenzene are only slightly luminescent. The fluorescence of a substituted *p*-dimethoxybenzene containing the grouping $C_6H_3(OMe)_2 \cdot C^{11} \cdot C^{12}$, is lessened or hindered by the introduction of a phenyl group in position 1¹, but is increased by a phenyl group in position 1². This is explained by means of Thiele's theory of partial valencies, and the conclusion drawn that a carbonyl group, or a group containing an ethylene linking, functions as a fluorogen the more strongly the more the partial valencies of the group are rendered inactive by the partial valency of the luminophore or benzene ring.

[With ADOLF GROMBACH.]—2:5-Dimethoxybenzophenone, $C_{15}H_{14}O_3$, is formed together with a small quantity of 5-hydroxy-2-methoxybenzophenone by the action of benzoyl chloride on *p*-dimethoxybenzene in carbon disulphide solution in presence of aluminium chloride; it separates from methyl alcohol or light petroleum in yellow crystals, melts at 51°, boils at 225° under 30 mm. pressure, is readily soluble in most solvents, dissolves without decomposing in concentrated sulphuric acid, forming a brownish-red solution, and yields benzoic acid and *p*-dimethoxybenzene when fused with potassium hydroxide. The phenylhydrazone, $C_6H_3(OMe)_2 \cdot CPh \cdot N_2HPh$, formed by shaking the dimethyl ether with phenylhydrazine in glacial acetic acid solution, separates from alcohol in white crystals and melts at 126°. When boiled with hydroxylamine hydrochloride in alcoholic solution, the dimethyl ether yields two stereoisomeric oximes: the oxime



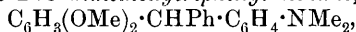
melts at 136° and is less soluble in aqueous sodium hydroxide than the more strongly acid stereoisomeride, $C_6H_3(OMe)_2 \cdot \underset{\substack{| \\ OH \cdot N}}{C} \cdot Ph$, which melts at 120°.

5-Hydroxy-2-methoxybenzophenone, $C_{14}H_{12}O_3$, formed by hydrolysis

of the dimethyl ether with aluminum chloride at 70—80°, or with boiling concentrated hydriodic acid, separates from alcohol in large, stout, yellow crystals, melts at 78°, and when shaken with methyl sulphate and aqueous sodium hydroxide yields the dimethyl ether. The *phenylhydrazone*, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CPh}\cdot\text{N}_2\text{HPh}$, formed by the action of phenylhydrazine on the monomethyl ether in glacial acetic acid solution, crystallises from alcohol in colourless needles and melts at 144°.

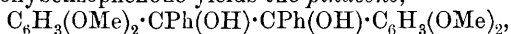
2:5-Dimethoxybenzophenone dichloride (*2:5-dimethoxydiphenyldichloromethane*), $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CPhCl}_2$, is formed by the action of phosphorus pentachloride on 2:5-dimethoxybenzophenone on the water-bath; it crystallises in colourless prisms, decomposes gradually on exposure to air, is moderately stable towards cold water, but is hydrolysed rapidly by boiling water, and gives an intense green coloration with aluminium chloride in benzene solution. When heated with aniline, it forms *2:5-dimethoxybenzophenonephenylimine*, $\text{CPh}(\text{OMe})_2\cdot\text{C}_6\text{H}_3\cdot\text{NPh}$, which crystallises from alcohol in long, lemon-yellow needles, melts at 146°, and is hydrolysed by cold dilute hydrochloric acid, with formation of aniline and dimethoxybenzophenone.

4'-Dimethylamino-2:5-dimethoxytriphenylmethane,



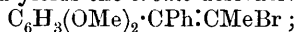
is prepared by heating 2:5-dimethoxybenzophenone dichloride with dimethylaniline on the water-bath; it separates from alcohol in colourless crystals, melts at 112°, and is soluble in dilute mineral acids.

When reduced with zinc dust in boiling glacial acetic acid solution, 2:5-dimethoxybenzophenone yields the *pinacone*,



which crystallises in long, glistening, silky needles and melts at 162°.

2:5-Dimethoxydiphenylethylcarbinol, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CETPh}\cdot\text{OH}$, is prepared by the action of dimethoxybenzophenone on magnesium ethyl bromide and treatment of the product with ice-water; it separates from light petroleum in large, transparent crystals, melts at 56°, boils at 230° under 30 mm. pressure, is readily soluble in ether, chloroform, carbon disulphide, acetone, glacial acetic acid, or benzene, gives a dark blue coloration with concentrated sulphuric acid or phosphoric acid, and when boiled with 60 per cent. sulphuric acid decomposes and forms a solution with violet fluorescence. When treated with hydrogen chloride in ethereal solution cooled by ice, the carbinol yields the *chloride* as an oily liquid, which, when heated on the water-bath, loses hydrogen chloride and forms *2:5-dimethoxy- α -diphenylpropylene*, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CPh}\cdot\text{CHMe}$; this is formed also by boiling the carbinol with acetyl chloride in benzene solution in a reflux apparatus. It is a liquid which boils at 198° under 12 mm. pressure, gives a bluish-violet coloration with concentrated sulphuric acid, and decomposes, forming a solution with intense violet fluorescence, when boiled with 60 per cent. sulphuric acid. With bromine in chloroform solution, it forms an unstable *dibromide*, which on evaporation loses hydrogen bromide and yields the *bromo-derivative*,



this crystallises from light petroleum and melts at 81.5°.

2:5-Dimethoxydiphenylmethylcarbinol, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CPhMe}\cdot\text{OH}$, is

prepared in the same way as the ethylcarbinol ; it separates from light petroleum in transparent crystals, melts at 65° , is readily soluble in most solvents, and gives a blue coloration with concentrated sulphuric acid. When treated with hydrogen chloride, it yields 2:5-dimethoxy- α -phenylstyrene, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CPh}\cdot\text{CH}_2$, which is obtained as a light yellow oil boiling at $206\text{--}207^{\circ}$ under 21 mm. pressure. It dissolves in benzene or acetone, forming a solution with slight fluorescence, and with bromine in chloroform solution forms a *dibromide* which readily loses hydrogen bromide.

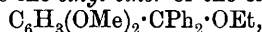
2:5-Dimethoxydiphenylbenzylcarbinol,



crystallises from alcohol in long, white needles, melts at 110° , is readily soluble in carbon disulphide, chloroform, or benzene, and gives a greenish-brown coloration with concentrated sulphuric acid.

2:5-Dimethoxyphenylstilbene, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CPh}\cdot\text{CHPh}$, separates from light petroleum in large, white crystals, melts at $82\cdot5^{\circ}$, and is sparingly soluble in alcohol or light petroleum, but is readily so in the other ordinary solvents. It unites with bromine to form a *dibromide*, which readily loses hydrogen bromide, forming the *bromo-derivative*, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CPh}\cdot\text{CPhBr}$; this crystallises from a mixture of benzene and light petroleum and melts at 118° .

2:5-Dimethoxytriphenylcarbinol, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CPh}_2\cdot\text{OH}$, is prepared by the action of magnesium phenyl bromide on dimethoxybenzophenone or on ethyl 2:5-dimethoxybenzoate ; it crystallises from alcohol, melts at 141° , is readily soluble in chloroform, benzene, or glacial acetic acid, and gives an emerald-green coloration with concentrated sulphuric acid. If a current of hydrogen chloride is passed through a solution of the carbinol in benzene containing anhydrous sodium sulphate, there is formed 2:5-dimethoxytriphenylmethyl chloride, $\text{C}_{21}\text{H}_{19}\text{O}_2\text{Cl}$, which crystallises in white needles and melts at 98° . When boiled with sodium ethoxide in absolute alcoholic solution, the chloride forms the *ethyl ether* of the carbinol,



which separates from alcohol in large, white crystals, melts at $85\text{--}86^{\circ}$, and dissolves in concentrated sulphuric acid, forming an emerald-green solution.

2:5-Dimethoxytriphenylmethane, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CHPh}_2$, is formed by boiling the carbinol or its chloride or ethyl ether with hydrogen chloride in alcoholic solution, or by reducing the carbinol with zinc dust and boiling glacial acetic acid ; it crystallises from alcohol in white needles melting at 104° , or from the super-cooled, concentrated alcoholic solution in leaflets melting at 84° , and gives a yellow coloration with concentrated sulphuric acid.

The *dimethyl ether* of phenylacetylquinol (2:5-dimethoxydeoxybenzoin), $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$, is formed together with a small quantity of the *monomethyl ether* by the action of phenylacetyl chloride and aluminium chloride on *p*-dimethoxybenzene in cooled carbon disulphide solution ; it separates from light petroleum in light yellow crystals, melts at 49° , boils at $226\text{--}227^{\circ}$ under 16 mm. pressure, gives an intense orange coloration with concentrated sulphuric acid, and dissolves in *isobutyl* alcohol forming a solution with violet-blue, in

benzyl alcohol forming a solution with a less intense blue, and in ethyl or methyl alcohol forming a solution with slight blue, fluorescence.

The *phenylhydrazone* forms an oil. The ketone interacts with magnesium phenyl bromide, forming 2:5-dimethoxydiphenylbenzylcarbinol, melting at 110°.

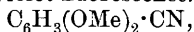
2:5-Dimethoxy- α -benzylstilbene, $C_6H_3(OMe)_2 \cdot C(CH_2Ph):CHPh$, formed by the action of magnesium benzyl chloride on 2:5-dimethoxydeoxybenzoin, is a viscid, yellow oil, which boils at 278° under 15 mm. pressure, dissolves in the usual solvents, forming solutions with violet or blue fluorescence, and with bromine forms slowly an *additive* compound, losing hydrogen bromide at the laboratory temperature.

2:5-Dimethoxypalmitylbenzene, $C_6H_3(OMe)_2 \cdot CO \cdot C_{15}H_{31}$, formed by the action of palmityl chloride and aluminium chloride on *p*-dimethoxybenzene in carbon disulphide solution, separates from alcohol in white crystals, melts at 44°, gives an orange coloration with concentrated sulphuric acid, and dissolves in ethyl or isobutyl alcohol forming a solution with violet, in methyl or benzyl alcohol forming a solution with weak blue, fluorescence.

The *phenylhydrazone*, $C_{30}H_{46}O_2N_2$, separates from alcohol in white crystals, becomes brown when exposed to air, melts at 64°, and forms solutions which are not fluorescent.

Ethyl 2:5-dimethoxyphenylglyoxylate, $C_6H_3(OMe)_2 \cdot CO \cdot CO_2Et$, formed from ethoxalyl chloride and *p*-dimethoxybenzene, crystallises from light petroleum in slightly yellow leaflets, melts at 38°, boils at 200° under 11 mm. pressure, and is readily soluble in the usual solvents, forming yellow solutions in alcohol and glacial acetic acid.

2:5-Dimethoxybenzamide, $C_6H_3(OMe)_2 \cdot CO \cdot NH_2$, is formed by the action of carbamic chloride and aluminium chloride on *p*-dimethoxybenzene in carbon disulphide solution; it crystallises from water in long, glistening needles, melts at 140°, is readily soluble in benzene, chloroform, acetone, or boiling water, and gives a coloration with concentrated sulphuric acid; the alcoholic, glacial acetic acid, and aqueous solutions have a violet fluorescence. The *nitrile*,



formed by heating the amide with phosphorus pentachloride on the water-bath, crystallises from alcohol in white needles, melts at 82°, and has a slight violet fluorescence in alcoholic or glacial acetic acid solution.

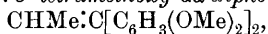
Dicyanodimethoxybenzene, $C_{10}H_8O_2N_2$, is formed by the action of an excess of methyl sulphate and aqueous sodium hydroxide on dicyanoquinol (Thiele and Meisenheimer, Abstr., 1900, i, 299); it crystallises from alcohol in slightly yellow needles, melts at 280—281°, is only sparingly soluble in the usual solvents, and when dissolved in alcohol or glacial acetic acid has an intense violet, in acetone or benzene a weaker violet, fluorescence. The luminescence of dicyanoquinol is greatly increased by the methylation of the two hydroxyl groups.

2:5-Dimethoxybenzoic acid (Tiemann and Müller, Abstr., 1882, 52), formed by hydrolysis of its amide, dissolves in glacial acetic acid or alcohol, forming a solution having an intense violet fluorescence; the aqueous solution has a violet fluorescence which is diminished by addition

of an alkali hydroxide. The *ethyl* ester, $C_6H_3(OMe)_2 \cdot CO_2Et$, formed by the action of hydrogen chloride on the acid in alcoholic solution, is a colourless liquid which boils at $167-168^\circ$ under 14 mm. or at 285° under the atmospheric pressure, has the sp. gr. 1.1443 at $26^\circ/26^\circ$, and when dissolved in alcohol or glacial acetic acid has an intense, in other solvents a weaker, violet fluorescence; it gives a blue luminescence when acted on by the Tesla rays. The ester interacts with magnesium phenyl bromide to form 2:5-dimethoxytriphenylcarbinol.

2:5:2':5'-*Tetramethoxybenzophenone*, $CO[C_6H_3(OMe)_2]_2$, is formed by the successive action of phosphorus pentachloride and of *p*-dimethoxybenzene and aluminium chloride on 2:5-dimethoxybenzoic acid in carbon disulphide solution; it separates from alcohol in slightly yellow crystals, melts at 109° , is readily soluble in benzene, chloroform, or acetone, forms a yellow solution in alcohol or glacial acetic acid, and gives a coloration with concentrated sulphuric acid, but is not fluorescent. The *phenylhydrazone*, $C_{23}H_{24}O_4N_2$, forms white crystals and melts at 170° . The *oxime*, $C_{17}H_{19}O_5N$, is colourless, melts at 134.5° , and when treated with phosphorus pentachloride in ethereal solution is converted into 2:5-dimethoxybenzoyl-2:5-dimethoxyanilide, $C_6H_3(OMe)_2 \cdot CO \cdot NH \cdot C_6H_3(OMe)_2$. This crystallises in white needles, melts at 120° , and is not fluorescent (compare Bargellini, Abstr., 1905, i, 210).

The action of 2:5:2':5'-tetramethoxybenzophenone on magnesium ethyl bromide leads to the formation of 2:5:2':5'-tetramethoxydiphenylethylcarbinol, $CEt[C_6H_3(OMe)_2]_2 \cdot OH$, which separates from light petroleum in colourless crystals, melts at 120° , is readily soluble in benzene, chloroform, or glacial acetic acid, and gives a blue coloration with concentrated sulphuric acid. When treated with hydrogen chloride in benzene solution in presence of calcium chloride, the carbinol yields 2:5:2':5'-tetramethoxy-*aa*-diphenylpropylene,



which melts at 87° , gives a blue coloration with concentrated sulphuric acid, and is slightly fluorescent in acetone solution; with bromine, it forms an unstable *additive* compound, which readily loses hydrogen bromide. G. Y.

Certain Derivatives of Tetrabromo-*o*-benzoquinone. C. LORING JACKSON and FREDERICK W. RUSSE (*Amer. Chem. J.*, 1906, 35, 154-187).—By the action of cold acetone on tetrabromo-*o*-benzoquinone, hexabromo-*o*-quinocatechol ether (Jackson and Koch, Abstr., 1901, i, 597), hexabromo-*o*-dihydroxycatechol ether (*loc. cit.*), and heptabromo-*o*-quinocatechol hemiether are produced. Any of these substances can be obtained as the chief product of the reaction by careful adjustment of the conditions.

*Heptabromo-*o*-quinocatechol hemiether*, $OH \cdot C_6Br_4 \cdot O \cdot C_6Br_3O_2$, crystallises from benzene in large, square, yellow plates or prisms which effloresce on exposure to the air; it darkens between 200° and 240° , melts and decomposes at $244-245^\circ$, and is soluble in hot benzene, chloroform, ether, or nitrobenzene. The compound dissolves in ethyl alcohol, but, if the solution is warmed, decomposition occurs with formation of hexabromo-*o*-quinocatechol ether. When heptabromo-*o*-

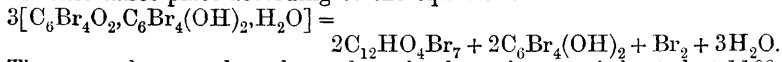
quinocatechol hemiether is reduced with zinc and dilute acetic acid, hexabromodihydroxycatechol ether is produced. By the action of benzoyl chloride on the hemiether, *tribenzoylheptabromodihydroxycatechol hemiether*, $\text{OBz} \cdot \text{C}_6\text{Br}_4 \cdot \text{O} \cdot \text{C}_6\text{Br}_3(\text{OBz})_2$, is obtained, which crystallises from benzene in small, flat, transparent plates, melts at $294-296^\circ$, and is soluble in benzene, sparingly so in alcohol, and insoluble in water.

When tetrabromo-*o*-benzoquinone is heated with benzoyl chloride, a compound is obtained which agrees in composition with tetrabromocatechol dibenzoate, but melts at $172-174^\circ$ instead of 197° . *Tetrabromocatechol dibenzoate*, $\text{C}_6\text{Br}_4(\text{OBz})_2$, obtained by heating tetrabromocatechol with benzoyl chloride for seven hours, crystallises in square, transparent plates, melts at 197° , and is soluble in benzene or chloroform and slightly so in alcohol. When tetrabromocatechol is heated with benzoyl chloride for only five to ten minutes, a compound is obtained which forms long, white needles, melts at $215-216^\circ$, and is probably impure tetrabromocatechol monobenzoate.

When tetrabromo-*o*-benzoquinone is left in contact with acetophenone, the same three products are obtained as are formed by the action of acetone, together with some ω -bromoacetophenone. Diethyl ketone and mesityl oxide react with the quinone in a similar manner. When a few drops of bromine are added to a mixture of acetone and tetrabromo-*o*-benzoquinone, hexabromo-*o*-quinocatechol ether and heptabromo-*o*-quinocatechol hemiether are produced, but very little of the hexabromodihydroxycatechol ether is formed. In corresponding experiments with hexabromo-*o*-quinocatechol ether, the dihydroxy-compound is obtained in brown plates and also in white, fibrous needles, and it is proved that the two products are identical in spite of the difference in their appearance.

When tetrabromo-*o*-benzoquinone is treated with heptaldehyde or benzaldehyde, hexabromo-*o*-quinocatechol ether and heptabromo-*o*-quinocatechol hemiether are produced.

By the action of tetrabromocatechol on tetrabromo-*o*-benzoquinone, Zincke (Abstr., 1887, 808) obtained a black compound which he did not study closely. This compound is now found to be *octabromo-*o*-quinhydrone*, $\text{C}_6\text{Br}_4\text{O}_2 \cdot \text{C}_6\text{Br}_4(\text{OH})_2 \cdot \text{H}_2\text{O}$; it crystallises in lustrous, black needles or slender prisms, and is soluble in ether, chloroform, or benzene, and insoluble in water. The quinhydrone cannot be purified by crystallisation from benzene, as in this solvent the substance gradually decomposes into heptabromo-*o*-quinocatechol hemiether and tetrabromocatechol. The decomposition of the compound with boiling benzene takes place according to the equation:



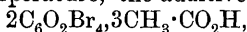
The same change takes place when the dry substance is heated at 110° .

Tetrabromocatechol diacetate forms colourless plates, melts at $215-216^\circ$, and is soluble in chloroform, alcohol, benzene, or ether.

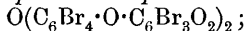
By the action of warm acetic acid on tetrabromo-*o*-benzoquinone, Jackson and Koch (Abstr., 1901, i, 598) obtained a white substance, $\text{C}_{14}\text{H}_2\text{O}_5\text{Br}_8$, which melted at 230° . Jackson and Porter (Abstr., 1904, i, 255) could not obtain this substance, but isolated a yellow product

melting at 244—245°. Further attempts to prepare the substance described by Jackson and Koch have resulted in the formation of hexabromo-*o*-quinocatechol ether. In one experiment, a yellow, crystalline substance melting at 235—250° was obtained, whilst in another experiment, in which the tetrabromo-*o*-benzoquinone was heated for a longer time with acetic acid at 100°, heptabromo-*o*-quinocatechol hemiether was produced.

When tetrabromo-*o*-benzoquinone is left in contact with glacial acetic acid at the ordinary temperature, the additive compound,



is obtained, which crystallises in white, rhombic plates, gradually becomes red when heated, but does not melt below 300°, and is soluble in alcohol, ether, benzene, or chloroform. On repeated crystallisation from benzene, the substance is converted into the yellow compound, melting at 235—250°, which was obtained by the action of hot acetic acid, and is probably *diheptabromo-o-quinocatechol ether*,



this substance is also formed by the action of formic acid on tetrabromo-*o*-benzoquinone. Propionic acid, butyric acid, and *isovaleric* acid seem to react with tetrabromo-*o*-quinone with formation of the same compound.

An attempt was made to prepare an additive compound of tetrabromo-*o*-benzoquinone with bromine, but without success. On heating the quinone with fuming nitric acid and bromine, two compounds were obtained, one yellow, the other white. The yellow substance, which is probably *tetrabromocyclopentene-o-quinone*, $\text{CBr} \begin{smallmatrix} \text{CBr} \text{---} \text{CO} \\ \text{CBr}_2 \cdot \text{CO} \end{smallmatrix}$, crystal-

lises in plates or prisms, melts at 142°, is soluble in alcohol, ether, chloroform, benzene, or acetone, and when treated with *o*-diamines gives a deep red colour characteristic of quinoxalines of this class. The white compound crystallises in needles, melts at 144—146°, is very soluble in water, and has an acid reaction.

By the action of *o*-phenylenediamine or 4:6-dibromo-*o*-phenylenediamine on tetrabromo-*o*-benzoquinone, a dark red, amorphous product is formed. When tetrabromo-*o*-benzoquinone is treated with potassium phenoxide or sodium alkylloxides, brown or red amorphous products are obtained.

E. G.

1:4-Anthraquinone. HANS DIENEL (*Ber.*, 1906, 39, 926—933. Compare *Abstr.*, 1905, i, 767).—**2-Nitroso-1-anthrol.**—The zinc salt, $(\text{O}:\text{C}_{14}\text{H}_8:\text{N} \cdot \text{O})_2\text{Zn}$, obtained by heating an alcoholic solution of 1-anthrol with sodium nitrite and a concentrated aqueous solution of zinc chloride, is a dark red, crystalline powder. By the action of a hot dilute solution of sodium hydroxide, 2-nitroso-1-anthrol is prepared. It crystallises in reddish-brown or orange needles, decomposes at about 200°, and develops a violet-red colour with concentrated sulphuric acid. The potassium salt crystallises in yellow needles or leaflets and is decomposed by water. The ethyl ether, $\text{O}:\text{C}_{14}\text{H}_8:\text{N} \cdot \text{OEt}$, obtained from the silver salt and ethyl iodide, crystallises in glistening, yellow needles and melts at 144°. The methyl ether melts at 134°. 2-Amino-1-anthrol hydrochloride is obtained by the reduction of 2-nitroso-1-anthrol or its

salts by stannous chloride and hydrochloric acid; it readily oxidises in the air, and by acetylation yields *triacetyl-2-amino-1-anthrol*, $\text{OAc} \cdot \text{C}_{14}\text{H}_8 \cdot \text{N} \cdot \text{Ac}_2$, which crystallises in glistening, green leaflets or needles and melts at 161° . Each of the two compounds just mentioned is readily oxidised to 1:2-anthraquinone by ferric chloride in the presence of hydrochloric acid.

4-Nitroso-1-anthrol separates after some time from the reddish-brown mother liquor from which the zinc salt of 2-nitroso-1-anthrol is obtained; it forms glistening, brown needles, which darken at 205° and melt and decompose at 233° . The *potassium* and *sodium* salts are yellowish-brown substances which are readily decomposed by water or alcohol. 4-Nitroso-1-anthrol dissolves in concentrated sulphuric acid with a characteristic indigo-blue coloration.

1:4-Anthraquinone is obtained by the reduction of 4-nitroso-1-anthrol, followed by the oxidation of the stannochloride so produced with ferric chloride. It crystallises in long, yellow needles, melts at 206° , readily sublimes, and is volatile in steam. Its constitution is proved by simultaneous reduction and acetylation to diacetyl-1:4-anthraquinol, from which diacetylquinizarin is obtained by oxidation with chromic and acetic acids. The last compound is hydrolysed to quinizarin by alcoholic potassium hydroxide.

Anthracene-1-nitrile obtained by distilling a mixture of anthracene-1-sulphonate with powdered potassium cyanide, crystallises in glassy, yellow leaflets and melts at 126° .

Anthraquinone-1-nitrile, $\text{C}_{14}\text{H}_9\text{O}_2 \cdot \text{CN}$, obtained by the oxidation of the preceding compound or by the distillation of anthraquinone-1-sulphonate and potassium cyanide, crystallises in golden-yellow leaflets and melts at $216\text{--}217^\circ$. After prolonged hydrolysis, these two nitriles are converted into the corresponding acids. *Anthracene-1-carboxylic chloride*, $\text{C}_{14}\text{H}_9 \cdot \text{COCl}$, is stable in the presence of water. The *amide*, $\text{C}_{14}\text{H}_9 \cdot \text{CO} \cdot \text{NH}_2$, obtained by passing ammonia into a benzene solution of the chloride, crystallises in colourless needles or leaflets and melts at 256° . *Anthraquinone-1-carboxylamide* melts at 260° . C. S.

Diaminoanthraquinones. EMILIO NOELTING and W. WORTMANN (*Ber.*, 1906, **39**, 637—646).—The mixture of amines obtained by boiling gently Römer's mixed dinitroanthraquinones (*Abstr.*, 1883, 737) with aqueous sodium sulphide for some hours is boiled with dilute sulphuric acid and filtered. The insoluble sulphate, after recrystallisation from moderately concentrated sulphuric acid, yields Römer's 1:5-diaminoanthraquinone melting at 319° (*loc. cit.*); it dissolves in boiling dilute oxalic acid and crystallises out unchanged on cooling. 1:5-Dibenzoylaminoanthraquinone, $\text{C}_{14}\text{H}_6\text{O}_2(\text{NHBz})_2$, formed by boiling Römer's base with benzoyl chloride and dimethylaniline, melts above 350° .

The bases present in the sulphuric acid filtrate from the sulphate of Römer's base are precipitated by dilution with much water and converted into their acetyl derivatives by boiling with acetic anhydride and acetic acid, when on cooling there crystallises out 1:8-diacetyl-aminoanthraquinone, $\text{C}_{14}\text{H}_6\text{O}_2(\text{NHAc})_2$, which forms brownish-yellow

needles and melts at 284° ; the more soluble isomerides remain in solution. 1:8-*Diaminoanthraquinone*, $C_{14}H_6O_2(NH_2)_2$, obtained by treating the diacetyl derivative with ammonia or by heating anthraquinone-1:8-disulphonic acid with ammonia, crystallises from alcohol, glacial acetic acid, nitrobenzene, or pyridine, melts at 262° , is more readily soluble than the 1:5-isomeride, and has feeble basic properties. The *sulphate*, $C_{14}H_6O_2(NH_2)_2 \cdot H_2SO_4$, crystallises in glistening, black needles; the *hydrochloride*, $C_{14}H_6O_2(NH_2)_2 \cdot HCl$, forms a reddish-brown, amorphous mass. 1:8-*Dibenzoylaminoanthraquinone*, $C_{14}H_6O_2(NHBz)_2$, crystallises in glistening, yellow needles and melts at 324° . The *diacetyl* derivative melts at 284° .

When treated in the above manner, Böttger and Petersen's α -diaminoanthraquinone melting at 236° (this Journal, 1873, 26, 389) is found to be a mixture of 1:5- and 1:8-diaminoanthraquinones, together with isomerides forming more soluble acetyl derivatives.

2:7-Diaminoanthraquinone (β -diaminoanthraquinone: Schmidt, this Journal, 1874, 27, 987), formed by reduction of β -dinitroanthraquinone with sodium sulphide, crystallises from nitrobenzene or alcohol in orange-yellow needles and melts above 330° . The *sulphate*,

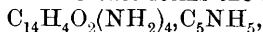


crystallises in colourless needles, becomes red on exposure to air, and is hydrolysed by much water; the *hydrochloride*, $C_{14}H_6O_2(NH_2)_2 \cdot HCl$, was analysed; the *diacetyl* derivative, $C_{14}H_6O_2(NHAc)_2$, crystallises from nitrobenzene and melts above 350° . When diazotised and coupled with α -naphtholsulphonic acid, the 2:7-diamine forms a *derivative*, which dyes cotton wool directly but not intensely; when treated with nitrosyl sulphate in sulphuric acid solution and boiled with water, the diamine forms *isoanthraflavic acid*. *Methyl isoanthraflavate*, formed by the action of methyl sulphate and potassium hydroxide on the acid, crystallises from glacial acetic acid and melts at 214° .

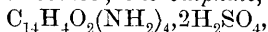
When heated with oxalic acid at 150 – 160° , 1-aminoanthraquinone forms the *oxamic acid*, $C_{14}H_7O_2 \cdot NH \cdot C_2O_3H$, which melts at 226° , and, when treated with nitric acid in sulphuric acid solution, yields 4-nitro-1-aminoanthraquinone (D.R.-P. 125391; Abstr., 1902, i, 382) melting at 296° . On reduction with sodium sulphide, it yields 1:4-*diaminoanthraquinone*, $C_{14}H_6O_2(NH_2)_2$, which crystallises from alcohol, melts at 268° , and dissolves in sulphuric or hydrochloric acid, forming a red solution. 1:4-*Diacetylaminoanthraquinone*, $C_{14}H_6O_2(NHAc)_2$, forms reddish-yellow needles and melts at 271° .

When heated with oxalic acid at 150 – 160° , 1:5-diaminoanthraquinone forms the *dioxamic acid*, $C_{14}H_6O_2(NH \cdot C_2O_3H)_2 \cdot 2H_2O$, which is obtained as a yellow powder; it loses $2H_2O$ at 140 – 150° , becomes red at 250° , and decomposes at about 300° (D.R.-P. 158076); on nitration in sulphuric acid solution, it yields 4:8-dinitro-1:5-diaminoanthraquinone (Abstr., 1902, i, 476). This is reduced by sodium sulphide, forming 1:4:5:8-tetra-aminoanthraquinone, which melts at 332° , and, in dilute acetic acid solution, dyes cotton wool mordanted with tannin, but not silk, violet-blue; after treatment with methyl sulphate and sodium acetate in acetic acid solution, it dyes silk moderately, or cotton wool mordanted with tannin an intense, blue. A diagram is given showing the results of the spectroscopic examination of the tetra-amino-compound.

With pyridine, the tetra-amine base forms the *additive* compound,



which crystallises in red needles; the *sulphate*,



crystallises in needles; the *tetra-acetyl* derivative, $\text{C}_{14}\text{H}_4\text{O}_2(\text{NHAc})_4$, forms orange-red needles or thick, green, shimmering crystals, and melts above 330° .

When boiled with chlorodinitrobenzene and sodium acetate in alcoholic solution in a reflux apparatus, the tetra-amino compound yields the *product*, $\text{C}_{14}\text{H}_4\text{O}_2(\text{NH}_2)_3 \cdot \text{NH} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$, which crystallises in green, shimmering needles and does not melt at 340° . G. Y.

Blue and Green Anthracene Dyes. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 159129).—4-Bromo-1-methylamino-anthraquinone condenses with *p*-toluidine on boiling, and on cooling to 60° and adding methyl alcohol, dark blue crystals with coppery lustre of 4 *p*-toluidino-1-methylaminoanthraquinone separate. The product dissolves in chloroform or pyridine to bluish-green solutions. Aniline, *o*-toluidine, xylydine, or naphthylamine may replace the *p*-toluidine. Similar compounds are obtained from 4-bromo-1-methylamino-2-methyl-anthraquinone, dibromo-1:5-dimethyldiaminoanthraquinone or 4-bromo-1-methylaminoanthraquinonesulphonic acid. C. H. D.

Preparation of Aminohydroxyanthraquinonesulphonic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 161035).—When *p*-aminohydroxyanthraquinone or its alkyl derivatives are sulphonated, the sulpho-group enters the ring containing the amino- and hydroxy-groups. When, however, the boric esters are sulphonated, or when sulphonation is carried out in the presence of boric acid, heteronuclear sulphonic acids are obtained. The reaction takes place at 110 — 120° .

Unlike the homonuclear sulphonic acids, the products give characteristic colorations when boric acid is added to their solutions in concentrated sulphuric acid. C. H. D.

Compounds of Aniline with 1:2-Anthraquinone and a New Hydroxyanthraquinone. KASIMIR LAGODZINSKI (*Annalen*, 1906, 344, 78—92. Compare this vol., i, 98; Kehrmann, *Abstr.*, 1898, i, 439).—1:2-Anthraquinone dissolves in aniline at the laboratory temperature with development of heat and formation of 2-hydroxy-1:4-anthraquinone-4-anil, $\text{C}_8\text{H}_6 \begin{matrix} \text{CO} & \text{C} \cdot \text{OH} \\ & | \\ & \text{C}(\text{NPh}) \cdot \text{CH} \end{matrix}$, together with a small quantity of 2-anilino-1:4-anthraquinone-4-anil, which is removed by washing the product with alcohol and warm benzene. The anil, purified by solution in warm alcoholic potassium hydroxide, precipitation with acetic acid, and recrystallisation from benzene, forms matted, thin, glistening, fiery-red needles containing C_8H_6 , decomposes at about 255° , dissolves in concentrated sulphuric acid forming a brownish-red solution, is readily soluble in aqueous or alcoholic alkali hydroxides, and forms orange-yellow *alkali* salts. On reduction with glacial acetic

acid and zinc dust, the anilide forms a greenish-yellow solution which becomes reddish-brown when shaken with air, but if the reduction is effected with an excess of zinc dust and prolonged warming, a stable, dark green solution is obtained. On oxidation with a dilute solution of chromic acid in glacial acetic acid solution, the anil yields a product which separates in colourless crystals. The *additive* compound, $C_{20}H_{18}O_2N, C_2H_4O$, formed when the anil is heated with glacial acetic acid, crystallises in long, scarlet needles, does not melt at 250° , and dissolves on warming in dilute alkali hydroxides, forming orange-yellow solutions.

2-Methoxy-1:4-anthraquinone-4-anil, $C_8H_6 \begin{smallmatrix} \text{CO} \text{---} \text{C} \cdot \text{OMe} \\ | \\ \text{C}(\text{NPh}) \cdot \text{CH} \end{smallmatrix}$, formed by the action of methyl sulphate on the hydroxy-compound in alcoholic potassium hydroxide solution, crystallises in long, golden-yellow needles, melts at 175° , and is insoluble in aqueous alkali hydroxides, but dissolves in concentrated sulphuric acid, forming a brownish-red solution.

2-Anilino-1:4-anthraquinone-4-anil, $C_8H_6 \begin{smallmatrix} \text{CO} \text{---} \text{C} \cdot \text{NHPh} \\ | \\ \text{C}(\text{NPh}) \cdot \text{CH} \end{smallmatrix}$, is formed by warming 1:2-anthraquinone or 2-hydroxy-1:4-anthraquinone-4-anil with an excess of aniline on the water-bath; it crystallises from benzene in matted, fiery-red needles, melts at 230° , is soluble in alcohol or glacial acetic acid, and dissolves in concentrated sulphuric acid, forming an intense rosaniline-red solution. When warmed with zinc dust and glacial acetic acid, it is reduced to the greenish-yellow leuco-base, which is oxidised by air.

2-Hydroxy-1:4-anthraquinone, $C_8H_6 \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{OH} \\ | \\ \text{CO} \cdot \text{CH} \end{smallmatrix}$, is formed by heating finely-divided 2-hydroxy-1:4-anthraquinone-4-anil with equal volumes of concentrated hydrochloric acid and water in a sealed tube at $140\text{--}150^\circ$ for one hour; it crystallises from alcohol in long, thin, dark yellow or light brown needles, becomes brown at 230° , decomposes at about 235° , sublimes almost undecomposed in small, sulphur-yellow needles, and dissolves in aqueous alkali hydroxides or carbonates, or in concentrated sulphuric acid forming a red solution. The *alkali* salts are orange-yellow; with barium and calcium chlorides, the ammoniacal solution forms voluminous, orange-yellow *precipitates*; the *silver* salt is obtained as a reddish-yellow precipitate which, when warmed with an excess of ammonia, forms a characteristic silver mirror. 2-Acetoxy-1:4-anthraquinone, $C_{16}H_{10}O_2$, crystallises in light-yellow leaflets or sulphur-yellow needles and melts at 188° . G. Y.

Preparation of 1:4:8-Trihydroxyanthraquinone. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 161026).—When the method employed for the conversion of alizarin into 1:2:5-trihydroxyanthraquinone (Abstr., 1905, i, 532) is applied to chrysazin, 1:4:8-trihydroxyanthraquinone is obtained. The oxidation is carried out with sulphuric acid containing 80 per cent. anhydride and boric acid at $25\text{--}35^\circ$. In the absence of boric acid, higher oxidation products, up

to the hexahydroxy-compound, are obtained. Anthrarufin and quinzarin do not yield α -hydroxy-derivatives on similar treatment.

1 : 4 : 8-Trihydroxyanthraquinone separates from pyridine or nitrobenzene in brownish-red needles or leaflets with green reflex and dissolves in sodium hydroxide or concentrated sulphuric acid to violet solutions.
C. H. D.

Presence of Guaiol in an Odoriferous Wood from New Guinea. P. A. A. F. EYKEN (*Rec. trav. chim.*, 1906, 25, 40—43).—This wood, which has the vernacular name "Kajoe garoe," yields, on distillation with steam, an essential oil which is nearly solid at the ordinary temperature. The product obtained by exposing the oil on a filter paper and recrystallising the residue from alcohol forms brilliant, long prisms, melts at 93°, has $[\alpha]_D - 30^\circ$ at 17°, boils at 288—289°, and is identical with guaiol obtained from guaiacum wood (*Schimmel & Co.'s Berichte*, 1902, 1, 42; compare Wallach and Tuttle, *Abstr.*, 1894, i, 538). The crude oil, on distillation, yields formic and acetic acids and guaiol, and leaves a brown residue. If the oil is freed from acid and resinous matters by shaking its solution in ether with an alkali, it deposits guaiol after a time and leaves an oily liquid, which is dextrorotatory and is not separable into its constituents by fractional distillation. The botanical origin of the wood is unknown, but it appears to be derived from a conifer.
T. A. H.

Pure Nerol. HUGO VON SODEN and WALTER TREFF (*Ber.*, 1906, 39, 906—914).—Crude nerol, obtained from oil of petit-grain, is converted into the diphenylurethane derivative (compare H. and E. Erdmann, *Abstr.*, 1898, i, 35), and the mixture of neryl- and geranyl-diphenylurethanes is separated almost completely by fractional crystallisation from light petroleum (b. p. 30—40°) or methyl alcohol, in which the latter is much less soluble. In this way it is shown that nerol, which has been freed from geraniol as completely as possible by treatment with calcium chloride, still contains 25 to 30 per cent. of that substance.

From *d*- or *l*-linalool, nerol has been isolated in the form of its pure diphenylurethane which melts at 52—53° (compare Hesse and Zeitschel, *Abstr.*, 1903, i, 189). The action of acetic anhydride on linalool (*Chem. Ind.*, 1906, 29, 20) yields nerol which contains geraniol.

Pure nerol, prepared from the diphenylurethane by the action of an alcoholic solution of potassium hydroxide, is a colourless oil with the odour of roses; it boils at 125° under 25 mm. or at 224—225° under 755 mm. pressure, has a sp. gr. 0.8813 at 15°, and is optically inactive. The pure acetate boils at 93—94° under 3 mm. pressure, has the sp. gr. 0.916 at 15°, and the saponification number 286.2; the formate has not been obtained pure (compare Soden and Zeitschel, *Abstr.*, 1903, i, 267). The *tetrabromide*, $C_{10}H_{18}OBr_4$, crystallises in long needles and melts at 118—119°.

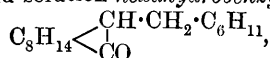
A dilute solution of chromic acid oxidises nerol to an aldehyde which is apparently citral *b*.

Pure geraniol boils at 229—230° under atmospheric pressure and at 94° under 3 mm., has the sp. gr. 0.8825 at 15°, and is optically

inactive. The tetrabromide, $C_{10}H_{18}OBr_4$, crystallises in small needles and melts at $70-71^\circ$. C. S.

Rotatory Powers of Hexahydrobenzylidenecamphor and α -Nanthyldenecamphor and the Corresponding Saturated Derivatives; Comparison of the Rotatory Powers of these Compounds with those of Benzylidenecamphor and Benzylcamphor. ALBIN HALLER and FRANCOIS MARCH (*Compt. rend.*, 1906, 142, 316—319. Compare Abstr., 1899, i, 770; ii, 622; 1900, i, 182; 1903, i, 503, 563, 628; 1904, i, 751; 1905, i, 602).

Hexahydrobenzylidenecamphor, $C_8H_{14} \begin{smallmatrix} \text{C} \cdot \text{CH} \cdot \text{C}_6\text{H}_{11} \\ | \\ \text{CO} \end{smallmatrix}$, obtained by the action of hexahydrobenzaldehyde on the sodium derivative of camphor (Abstr., 1904, i, 600; 1905, i, 214), forms large, colourless crystals, which melt at 49° ; it is readily soluble in ether or light petroleum and insoluble in water, and yields on reduction with sodium amalgam in acid solution *hexahydrobenzylcamphor*,



in the form of a colourless oil boiling at 192° under 24 mm. pressure.

Heptylcamphor (α -*nanthylcamphor*), $C_8H_4 \begin{smallmatrix} \text{CH} \cdot \text{C}_7\text{H}_{15} \\ | \\ \text{CO} \end{smallmatrix}$, prepared by the action of *n*-heptyl iodide on the sodium derivative of camphor in the presence of toluene, is a colourless oil boiling at 190° under 25 mm. pressure; it yields a bromo-derivative which, on boiling with diethyl-aniline, loses HBr and forms *heptylidenecamphor* (α -*nanthylidenecamphor*), $C_8H_4 \begin{smallmatrix} \text{C} \cdot \text{CH} \cdot \text{C}_6\text{H}_{13} \\ | \\ \text{CO} \end{smallmatrix}$, a colourless oil boiling at $180-182^\circ$ under 20 mm. pressure.

The specific rotations of these new camphor derivatives are given in the following table, in which is also included the corresponding constants of benzylidenecamphor and benzylcamphor for the purpose of comparison.

Rotatory Power of Unsaturated Series.		Rotatory Power of Saturated Series.	
Benzylidenecamphor	$[\alpha]_D + 425^\circ 11'$	Benzylcamphor	$[\alpha]_D + 144^\circ 00'$
Hexahydrobenzylidene-		Hexahydrobenzylcamphor	+ 55 07
camphor	+ 131 39	Heptylcamphor	+ 51 13
Heptylidenecamphor	+ 136 40		

These numbers show (1) that the specific rotations of the new compounds are much lower than the specific rotations of the corresponding benzenoid compounds, (2) that the rotation of the saturated derivative is lower than that of the corresponding unsaturated compound, (3) that the cyclic or aliphatic nature of the group C_6H_{11} or C_6H_{13} does not appreciably modify the rotatory power in the two series.

M. A. W.

Carvone Hydrate. EMIL KNOEVENAGEL and OSKAR SAMEL, *Ber.*, 1906, 39, 677—685. Compare Rupe and Schlochoff, Abstr., 1905, i, 449).—Carvone hydrate (8-hydroxy-8:9-dihydrocarvone) is formed

when carvone is boiled with 36.5 per cent. solution of sodium hydrogen sulphite until a clear solution is obtained, and the cold solution then treated with a mixture of equal parts of concentrated sulphuric acid and water, care being taken to avoid rise of temperature. After eight days, the carvone hydrate is precipitated by the addition of 25—30 per cent. sodium hydroxide solution. The yield is 80 per cent., and after crystallisation from a mixture of ether and light petroleum it melts at 42—43°.

When heated for three hours under reduced pressure, the hydrate is converted into carvacrol and carvone. It does not react with benzoyl chloride, phenylthiocarbimide, or hydrogen sulphide, nor does it yield a condensation product with benzaldehyde. The *phenylhydrazone*, $C_{10}H_{22}ON_2$, crystallises from alcohol in long, pale yellow needles and melts at 134—135°. The semicarbazone melts at 177—179° (Rupe and Schlochoff give 176°). When reduced with zinc dust in alkaline solution, the hydrate yields *dihydrocarvone hydrate* (8-hydroxymenthane-2-one), $CHMe \begin{smallmatrix} \text{CO-CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} CMe_2 \cdot OH$ (45 per cent. yield), which is also formed when Baeyer's glycol, dihydrocarveol hydrate (Abstr., 1895, i, 550), is oxidised with chromic acid in acetic acid solution. It distils at 138—139° under 9 mm. pressure, combines with sodium hydrogen sulphite, has a sp. gr. 1.006 at 19°/4°, n_D 1.476 at 20°, and $[\alpha]_D -18.5^\circ$ at 20°. The semicarbazone, $C_{11}H_{21}O_2N_3$, melts at 150.5—151°, whereas Baeyer and Henrich (*Ber.*, 1895, 28, 1590) give 139° as the melting point.

Dehydrating agents convert carvone hydrate into carvacrol and carvone, but when the hydrate is heated for one hour with potassium hydrogen sulphate it is transformed quantitatively into carvacrol.

J. J. S.

Composition of the Volatile Oil of *Backhousia citriodora* from Queensland (*Bull. Imp. Inst.*, 1905, 3, 11—13).—The volatile oil of *Backhousia citriodora* from Queensland is a greenish-yellow, transparent liquid, which has a strong odour of citral, a sp. gr. 0.8903 at 21°, n_D 1.4940 at 22°, and is optically inactive. It is miscible in all proportions with 80 per cent. alcohol, is completely soluble in 2.25 volumes of 70 per cent. alcohol, and contains 93.5 per cent. of citral. On distillation, 100 c.c. of the oil yields 10 c.c. boiling at 212—219°, 70 c.c. at 219—226°, and 10 c.c. at 226—231°.

A specimen of the oil of *Backhousia citriodora*, examined previously (*Schimmel's Berichte*, 1888, part I, 20), was stated to have a sp. gr. 0.900 and to consist largely of citral.

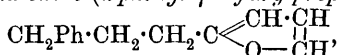
E. G.

Composition of the Ethereal Oil of the Carline Thistle (*Carlina acaulis* L.). FRIEDRICH W. SEMMLER (*Ber.*, 1906, 39, 726—731).—From the oil obtained by distillation of the dried roots of *Carlina acaulis* in a current of steam, the author had previously obtained the sesquiterpene, carlinene, $C_{15}H_{24}$, together with an oil containing oxygen and a crystalline solid (compare Gadamer, Abstr., 1903, i, 353).

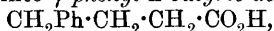
The carlina oil yielded on fractional distillation 12—15 per cent. of

carlinene, whilst palmitic acid was found in small amount. *Carlina oxide*, the principal constituent of the oil, was separated by repeated fractionation under diminished pressure; it boils at 167—168° under 20 mm. pressure, has a sp. gr. 1.066 at 17°/17° and n_D 1.586; it is optically inactive. Its probable formula is $C_{13}H_{10}O$. When oxidised by permanganate, it forms benzoic acid in large amount.

Tetrahydrocarlina oxide (α -phenyl- γ -2-furylpropane),



prepared by the reduction of carlina oxide with sodium and alcohol, is an oil which boils at about 135° under 10 mm. pressure and at about 262° (uncorr.) at the ordinary pressure. When oxidised by permanganate it is converted into γ -phenyl-*n*-butyric acid,



which crystallises in glistening leaflets, melts at 52°, and boils at about 165° under 10 mm. pressure; on further oxidation, this acid is converted into benzoic acid.

The presence of the furan ring in the molecule of tetrahydrocarlina oxide was shown by its synthesis from acetophenone and furfuraldehyde in the presence of alcoholic sodium ethoxide.

The conclusion is drawn that a furan ring, united with a phenyl group by a chain of three carbon atoms, is present in the molecule of carlina oxide.

A. McK.

Essence of the Wood of *Gonystylus miquelianus*.

P. A. A. F. EYKEN (*Rec. trav. chim.*, 1906, 25, 44—47).—The crude essence obtained by distilling the old wood in steam is a crystalline mass, melts at 66—68°, boils at 280—290°, and has $[\alpha]_D + 35^\circ$ in alcohol. By repeated crystallisation from acetic acid or alcohol, a sesquiterpene alcohol, *gonystylol*, $C_{15}H_{26}O$, was isolated. This, after distillation under reduced pressure, forms silky crystals, melts at 82°, boils at 164—166° under 17 mm. pressure, and has $[\alpha]_D + 30^\circ$ at 17° in alcohol. When heated with formic acid, it yields *gonystylene*, a colourless, mobile liquid, which boils at 137—139° under 17 mm. pressure, has a sp. gr. 0.9183 at 17°, $[\alpha]_D + 40^\circ$ at 17° in alcohol, and n_D 1.5134 at 15° (indicating the presence of two ethylenic linkings). No bromide, hydrochloride, hydrobromide, or corresponding alcohol could be prepared from gonystylene by the usual methods. It is pointed out that gonystylol and gonystylene have respectively the same specific rotations as guaïol (see this vol., i, 295) and guaïene, but in the opposite sense.

T. A. H.

Lemon-grass Oil from Montserrat (*Bull. Imp. Inst.*, 1904, 2, 166—167).—The oil of *Andropogon nardus*, var. *genuinus*, from Montserrat, is a clear, limpid, yellow liquid, with a pleasant, lemon-grass odour, and is soluble in 70 per cent. alcohol to the extent of 97 per cent. On distillation, about 25 per cent. of the oil is obtained between 180° and 220°, and 50 per cent., consisting principally of citral, between 220° and 230°. The oil has a sp. gr. 0.906 at 15°, $\alpha_D - 0.010'$ in a 100 mm. tube, and contains 74.6 per cent. of citral.

A sample of the oil, examined in the West Indies, had a sp. gr.

0.886 at 15°, $\alpha_D - 0^\circ 12.6'$ in a 100 mm. tube, and contained 74.2 per cent. of citral.

A comparison of this West Indian oil with the lemon-grass oil obtained in India from *Andropogon citratus* shows that the former contains as much citral as the latter, from which it only differs in being incompletely soluble in 70 per cent. alcohol. E. G.

New Ethereal Oils. RICHARD SCHMIDT and KARL WEILINGER (*Ber.*, 1906, 39, 652—658).—The oil from *Ocotea usambarensis* is limpid and of a yellow colour. It distils at 50—160° under 10 mm. pressure, some 75 per cent. passing over below 100°. It has a sp. gr. 0.913 at 20°, n_D 1.476, and $\alpha_D - 11^\circ 12'$ at 20°. It consists of myristaldehyde 1, cineol 40, *l*-terpineol 40, a *sesquiterpene*, $C_{15}H_{24}$ or $C_{15}H_{26}$, 10, esters 4 per cent., and a minute quantity of a *ketone* which yields a semicarbazone melting at 197°.

The oil from the leaves of *Piper volkensii* has a pale brown colour and an intense pleasant odour. It distils at 90—175° under 12 mm. pressure, has a sp. gr. 0.934 at 20°, n_D 1.5017, and $\alpha_D - 8^\circ 24'$. It contains 25 per cent. of limene (Burgess and Page, *Trans.*, 1904, 85, 414) and 45 per cent. of a compound, $C_{11}H_{12}O_3$, probably a methoxysafrole, $C_3H_5 \cdot C_6H_2(OMe) \langle \text{O} \rangle CH_2$, which distils at 136—140° under 12 mm. pressure, has a sp. gr. 1.137 at 20°, n_D 1.5416, but is optically inactive. Limene yields a *hexabromide*, $C_{15}H_{24}Br_6$, which crystallises from light petroleum and melts at 154°. The compound $C_{11}H_{12}O_3$ forms a *dibromide* which melts at 122° after recrystallisation from ethyl acetate. This may be transformed into the compound $C_{11}H_{12}O_3$ by means of zinc dust and acetic acid. J. J. S.

“Dande” Rubber from Rhodesia (*Bull. Imp. Inst.*, 1905, 3, 16—18).—Two samples of “Dande” rubber, derived from a species of *Landolphia*, from the Umtali District, Rhodesia, were examined. One of the samples was rather soft and sticky, somewhat deficient in tenacity, and had the following composition: moisture, 1.2 per cent.; resin, 7.0 per cent.; caoutchouc, 88.3 per cent.; dirt and insoluble matter, 3.5 per cent.; ash, 1.7 per cent. The other sample had very good physical properties and gave the following results on analysis: moisture, 15.5 per cent.; resin, 10.7 per cent.; caoutchouc, 68.1 per cent.; dirt and insoluble matter, 5.7 per cent.; ash, 1.6 per cent. E. G.

“Muteke” Rubber from North-Eastern Rhodesia (*Bull. Imp. Inst.*, 1905, 3, 14—16).—A specimen of “Muteke” rubber, probably derived from a new species of *Landolphia*, from North-Eastern Rhodesia, was found to have the following composition: moisture, 4.6 per cent.; resin, 12.0 per cent.; caoutchouc, 79.7 per cent.; dirt and insoluble matter, 3.7 per cent.; ash, 0.4 per cent. The product was of good elasticity and tenacity, and was completely soluble in benzene, chloroform, or carbon disulphide, and partially so in ether. E. G.

The Chemical Properties of the Copals. BOTTLER (*Chem. Rev. Fett. Harz. Ind.*, 1906, 13, 51—53).—The author has examined almost all the various copals found on the market, and finds that they belong to that class of resins which consist principally of resin acids or resin-oil acids. Substances which resist the action of alkalis, resens, are also present in varying amounts. Manila copal contains 12 per cent. of resen and Zanzibar copal 6 per cent., whilst the other copals contain still less.

W. P. S.

Empirical Formula and Properties of Solanin. GIOVANNI ROMEO (*Gazzetta*, 1905, 35, ii, 579—589. Compare Oddo and Colombano, Abstr., 1905, i, 455).—After quoting the analytical results for solanin obtained by previous investigators, the author describes a simple method for obtaining the glucoside in a pure state from the juice of the berries of *Solanum sodomæum*. The solanin prepared by the author turns brown at 280°, melts at 286°, and decomposes at a slightly higher temperature. This melting point, which is higher than that of any solanin previously extracted, is not changed by crystallising the compound from methyl alcohol (Oddo and Colombano, *loc. cit.*). Its analysis gives numbers corresponding with the formula $C_{36}H_{57}O_{13}N$ or $C_{36}H_{59}O_{13}N$. Its reactions are identical with those of solanin extracted from the potato, excepting as regards the coloration obtained with sulphuric acid of sp. gr. 1.835.

T. H. P.

Researches in the Pyran Series. EDMOND E. BLAISE and H. GAULT (*Compt. rend.*, 1906, 142, 452—454. Compare Abstr., 1904, i, 762).—The homologues of formaldehyde condense with ethyl oxalacetate in the presence of pyridine or diethylamine to form compounds which suffer simultaneous hydrolysis and dehydration by the action of cold concentrated sulphuric acid, and yield dianhydrides of the type $CHR[CH<\begin{smallmatrix} CO\cdot CO \\ CO\cdot O \end{smallmatrix}]_2$, from which the corresponding substituted diketopimelic acids are obtained by merely boiling with water. The dioximes of these acids are decomposed by boiling water to form the corresponding β -alkylglutaronitriles, whilst the acids themselves suffer dehydration by the action of sulphuric acid and yield the 4-alkylpyran-2:6-dicarboxylic acids, $CHR<\begin{smallmatrix} CH:C(CO_2H) \\ CH:C(CO_2H) \end{smallmatrix}>O$, the dibromides, $CHR<\begin{smallmatrix} CH:C(CO_2H) \\ CH:C(CO_2H) \end{smallmatrix}>OBr_2$, of which have no tendency to lose HBr and form xanthonium salts (compare Fosse, Abstr., 1903, i, 357; 1905, i, 607).

M. A. W.

Synthesis of Nencki and Sieber's Gallacetein. CARL BÜLOW and C. SCHMID (*Ber.*, 1906, 39, 850—857. Compare Bülow and Sautermeister, Abstr., 1904, i, 262; this vol., i, 201).—7:8-Di-hydroxy-2-o-m-p-trimethoxyphenyl-4-methylene-1:4-benzopyran hydrochloride, $C_6H_3(OH)_2<\begin{smallmatrix} O(HCl) \\ C(CH_2)\cdot CH \end{smallmatrix}>C\cdot C_6H_2(OMe)_3$, is readily formed when dry hydrogen chloride is passed into a solution of pyrogallol and 2:3:4-trimethoxybenzoylacetone in warm glacial acetic acid. It

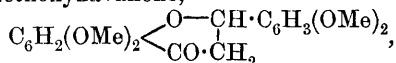
crystallises from alcohol containing a small amount of hydrochloric acid in red prisms melting and decomposing at 200–202°. The *sulphate*, $C_{19}H_{18}O_6 \cdot H_2SO_4$, dissolves readily in water and melts and decomposes at 124° after softening at 115°. The *picrate*, $C_{25}H_{21}O_{13}N_3$, crystallises from alcohol in red needles, melts and decomposes at 215°, and is sparingly soluble in the majority of solvents. The free base is obtained in the form of slender, violet-black needles when a hot aqueous solution of the hydrochloride is decomposed with an excess of sodium acetate solution. It melts at 183–185° and dissolves in alcohol, chloroform, carbon disulphide, or glacial acetic acid. The *diacetyl* derivative, $C_{23}H_{22}O_8$, crystallises from benzene in eosin-red needles.

When the hydrochloride of the trimethoxy-derivative is heated with concentrated hydrochloric acid at 150–180° for a day, it is hydrolysed to the hydrochloride of Nencki and Sieber's gallocetin, the colouring matter obtained from gallocetophenone (Abstr., 1881, 811), from which gallocetin itself may be prepared by the addition of ammonia.

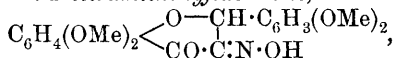
It has the constitution $C_6H_3(OH)_2 \left\langle \begin{array}{c} \text{O} \\ \text{C}(\text{CH}_2) \cdot \text{CH} \end{array} \right\rangle C \cdot C_6H_2(OH)_3$.

J. J. S.

Synthesis of Morin. STANISLAUS VON KOSTANECKI, VICTOR LAMPE, and JOSEF TAMBOR (*Ber.*, 1906, 39, 625–628. Compare Kostanecki and Tambor, *Abstr.*, 1904, i, 426).—A very small amount of 5 : 7 : 2' : 4'-tetramethoxyflavanone,



is formed when 2'-hydroxy-4' : 6' : 2 : 4-tetramethoxychalkone is boiled with aqueous alcoholic hydrochloric acid in a reflux apparatus. It crystallises from alcohol or carbon disulphide in white needles, melts at 167–168°, dissolves in alcoholic sodium hydroxide forming a yellow solution, and gives an orange coloration with concentrated sulphuric acid. When treated with amyl nitrite and hydrochloric acid, it forms 3-isonitroso-5 : 7 : 2' : 4'-tetramethoxyflavanone,



which crystallises in light yellow needles, decomposes at 199°, dyes the cobalt mordant yellow, and dissolves in aqueous sodium hydroxide, forming a light yellow solution. When boiled with sulphuric acid in glacial acetic acid solution, the isonitroso-compound yields *morin trimethyl ether*, $C_{15}H_5O_3(OH)_2(OMe)_3$, which crystallises in white needles, melts at 165°, and dissolves in aqueous sodium hydroxide to form a light yellow or in concentrated sulphuric acid to form a yellow solution having a green fluorescence, and dyes the alumina mordant light yellow.

When boiled with hydriodic acid of sp. gr. 1.9, 5 : 7 : 2' : 4'-tetramethoxyflavanone yields 5 : 7 : 2' : 4'-tetrahydroxyflavanol, which is identical with morin.

G. Y.

Action of Bromine on Cocaine. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1906, 25, 7).—When a solution of bromine in carbon

tetrachloride is added to a solution of cocaine in the same solvent, a yellow oil separates, which, on shaking out with water, slowly crystallises. This *substance* melts at 85° , has the composition

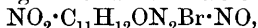


is soluble in ethyl acetate, slightly so in carbon tetrachloride, and insoluble in water and ether. It loses bromine somewhat readily, and when warmed with water evolves bromine and is converted into cocaine hydrobromide. A similar reaction is given by cinnamylcocaine.

T. A. H.

Cytisine. MARTIN FREUND and PAUL HORKHEIMER (*Ber.*, 1906, 39, 814—825. Compare Freund and Friedmann, *Abstr.*, 1901, i, 288; Freund, *Abstr.*, 1904, i, 263).—The mother liquors obtained in the preparation of α -nitronitrosocytisine, melting at 244 — 245° (Partheil, *Abstr.*, 1894, i, 558), contain the isomeric β -nitronitrosocytisine, $\text{NO}_2 \cdot \text{C}_{11}\text{H}_{12}\text{ON}_2 \cdot \text{NO}$, which melts and decomposes at 275° , and is less soluble than the α -isomeride in glacial acetic acid or alcohol. β -Nitrocytisine hydrochloride, $\text{C}_{11}\text{H}_{13}\text{ON}_2 \cdot \text{NO}_2 \cdot \text{HCl}$, formed by boiling the nitroso-compound with alcohol or aqueous hydrochloric acid, crystallises in long, golden-yellow needles, melts at 293° , and interacts with potassium nitrite in aqueous solution, forming β -nitronitrosocytisine. β -Nitrocytisine, $\text{C}_{11}\text{H}_{13}\text{O}_3\text{N}_3$, crystallises in matted, small needles or rosettes of long, slender needles and melts at 203° .

When a boiling solution of α -nitrocytisine is mixed with a hot solution of bromine in glacial acetic acid, an orange-red *perbromide* is formed; when boiled with alcohol containing sulphurous acid, this yields *bromo- α -nitrocytisine hydrobromide*, $\text{C}_{11}\text{H}_{13}\text{ON}_2\text{Br} \cdot \text{NO}_2 \cdot \text{HBr}$, which crystallises in yellow needles containing H_2O , melts at 235° , or, when anhydrous, at 286° , and interacts with potassium nitrite in aqueous solution, forming *bromo- α -nitronitrosocytisine*,



melting at 245° . *Bromo- α -nitrocytisine* crystallises in slender needles and melts at 135° ; the *hydrochloride*, $\text{C}_{11}\text{H}_{12}\text{O}_3\text{N}_3\text{Br} \cdot \text{HCl}$, crystallises in microscopic, slender needles and melts above 290° ; the *nitrate*, $\text{C}_{11}\text{H}_{12}\text{O}_3\text{N}_3\text{Br} \cdot \text{HNO}_3$, melts at 238° .

The action of nitric acid on dibromocytisine leads to the formation of *dibromonitrosocytisine*, $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_3\text{Br}_2$, which melts at 212 — 213° .

When reduced electrolytically in 50 per cent. sulphuric acid at 25 — 30° , with a lead beaker as cathode and a current of 5 amperes, cytisine yields *tetrahydrodeoxycytisine*, which is isolated in the form of its *hydrochloride*, $\text{C}_{11}\text{H}_{20}\text{N}_2 \cdot 2\text{HCl}$; this separates as a white, crystalline powder, melts at 282° , has $[\alpha]_D - 10^{\circ}15'$, and remains unchanged when heated with fuming hydrochloric acid or concentrated sulphuric acid. The *platinichloride*, $\text{C}_{11}\text{H}_{20}\text{N}_2 \cdot \text{H}_2\text{PtCl}_6$, forms hexagonal prisms and melts at 235° . The free *base* is an oil which boils at 270° under atmospheric pressure, has a strong spermic odour, is volatile with steam, blues litmus, absorbs carbon dioxide from the air, and is readily soluble in water. *Nitrosotetrahydrodeoxycytisine*, $\text{C}_{11}\text{H}_{19}\text{N}_2 \cdot \text{NO}$, formed when tetrahydrodeoxycytisine hydrochloride is boiled with concentrated nitric acid, crystallises in long needles, melts at 150° , and is readily converted into tetrahydrodeoxycytisine hydrochloride when

boiled with alcoholic hydrogen chloride. The action of phenylthiocarbimide on the base leads to the formation of the *thiocarbamide*, $C_{11}H_{19}N:N\cdot CS\cdot NHPh$, which crystallises in needles and melts at 108° .

When heated with methyl iodide, tetrahydrodeoxycytisine yields the *hydriodide*, $C_{11}H_{19}N:NMe, HI$, which crystallises in plates and melts at $205-206^{\circ}$; the free *methyl base* is volatile with steam. The *methiodide*, $C_{11}H_{19}N:NMe_2I$, crystallises in long leaflets or plates, melts at 283° , and dissolves in dilute hydrochloric acid, from its solution in which it is reprecipitated on addition of ammonia. *De-(N)-dimethyltetrahydrodeoxycytisine*, $C_{11}H_{18}N\cdot NMe_2$, is formed when the methiodide is treated with silver oxide and the *ammonium hydroxide* so obtained heated with aqueous potassium hydroxide; it is a light yellow oil, boils at $266-268^{\circ}$, and forms *salts* which are readily soluble in water.

The *methiodide*, $NMeI:C_{11}H_{18}\cdot NMe_2$, crystallises in plates and melts at $240-241^{\circ}$; the *dimethiodide*, $NMeI:C_{11}H_{18}\cdot NMe_2I$, melts at 293° , and when boiled with aqueous potassium hydroxide, evolves trimethylamine and yields a viscid oil boiling at $255-265^{\circ}$.

When treated with bromine in glacial acetic acid solution, tetrahydrodeoxycytisine yields a deep yellow *perbromide*, which is converted by boiling alcohol into the *hydrobromide*, $C_{11}H_{17}BrN_2\cdot 2HBr$; this crystallises in white needles, and, when recrystallised from absolute alcohol or hydrobromic acid, melts and decomposes at 206° , but after repeated recrystallisations from water, at about 280° . G. Y.

Alkylmeconines. E. MERMOD and HUGO SIMONIS (*Ber.*, 1906, **39**, 897—899. Compare this vol., i, 32).—When opianic acid undergoes the Grignard reaction, the yield of product is increased if constant stirring is maintained.

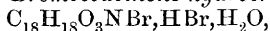
Ethylmeconine, $O\left\langle \begin{array}{c} CO---C:C(OMe) \\ CHEt:C:CH\cdot CH \end{array} \right\rangle C\cdot OMe$, prepared by the action

of magnesium ethyl iodide on opianic acid, separates from ethyl alcohol in monoclinic prisms and melts at 98° .

Propylmeconine, $C_{18}H_{16}O_4$, prepared by the action of magnesium propyl iodide on opianic acid, separates from ethyl alcohol in glistening needles and melts at 76° .

isoPropylmeconine, $C_{18}H_{16}O_4$, prepared from magnesium isopropyl iodide and opianic acid, separates from dilute alcohol in needles and melts at 61.5° . A. McK.

Thebaine. MARTIN FREUND (*Ber.*, 1906, **39**, 844—850. Compare *Abstr.*, 1905, i, 918).—*Bromocodeinone hydrobromide*,



is formed when a solution of bromine in glacial acetic acid is gradually dropped into an acetic acid solution of thebaine. It is sparingly soluble in water or alcohol and crystallises from a mixture of the two in large plates melting at $197-198^{\circ}$. It is not rendered anhydrous when heated at 130° in a current of hydrogen, and contains one methyl group attached to nitrogen and one to carbon. The *hydrochloride* crystallises with $2H_2O$ in the form of slender needles; these turn brown at 190° and melt at 194° . When dried at 150° , one mole-

cule of water is removed. *Bromocodeinone*, $C_{18}H_{18}O_3NBr$, crystallises from alcohol in needles which melt and decompose at $156-157^\circ$. It does not react with methyl iodide, and does not yield an acetyl derivative. When boiled with an aqueous solution of hydroxylamine hydrochloride, the hydrobromide of the base yields the *oxime* of *hydroxycodeinone*, $OH \cdot C_{18}H_{18}O_2N \cdot N \cdot OH$, which melts and decomposes at $272-273^\circ$ after recrystallisation from alcohol.

When reduced with sulphuric acid and iron filings, the hydrobromide yields Ach and Knorr's codeinone (Abstr., 1903, i, 849). J. J. S.

Strychnine Oxide. MAX MATTISSON (*Ber.*, 1906, 39, 705).—Polemical. The publication of the paper on strychnine oxide by Amé Pictet and Max Mattisson (Abstr., 1905, i, 816) took place without the knowledge and consent of the latter. The author disagrees with certain statements in the paper referred to. A. McK.

Action of Sulphuryl Chloride on Indole. Chloro- and Dichloro-indoles. GIROLAMO MAZZARA and ALESSANDRO BORGIO (*Gazzetta*, 1905, 35, ii, 563—569. Compare Abstr., 1905, i, 925).—*2-Chloroindole*, prepared by the action of sulphuryl chloride (1 mol.) on indole in ethereal solution, crystallises from light petroleum in silvery scales melting and decomposing at 91.5° . It has an irritant action on the skin and a faecal odour resembling that of scatole. It dissolves in concentrated sulphuric acid giving a green solution, and, in presence of dilute hydrochloric acid, is converted into oxindole. On heating with dilute potassium hydroxide solution, it becomes carbonised.

The action of sulphuryl chloride (2 mols.) on indole in ethereal solution yields 2:3-dichloroindole (compare Baeyer, Abstr., 1879, 535), which, when treated with potassium hydroxide and methyl iodide in methyl-alcohol solution, gives 2:3-dichloro-1-methylindole, $C_8H_4NMeCl_2$, crystallising from dilute alcohol in slender, silky needles melting at 58° . T. H. P.

Compounds of Palladic Chloride with [Tertiary] Cyclic [Bases]. RICHARD MÖHLAU (*Ber.*, 1906, 39, 861—863. Compare Gutbier, Abstr., 1905, i, 876; ii, 584; this vol., i, 12).—*tert*-Cyclic bases combine with palladic chloride yielding intensely coloured products, sparingly soluble in water or alcohol and insoluble in ether. Compounds of the type $PdCl_4 \cdot 2C_5NH_5 \cdot HCl$ have been prepared from the following bases. Pyridine, red prisms; 2-phenylpyridine, golden-yellow plates; quinoline, bright red prisms; 2-methylquinoline, red needles; 8-phenylquinoline, orange prisms; benzothiazole, orange-red prisms and plates. Tertiary alkaloids also yield coloured compounds. J. J. S.

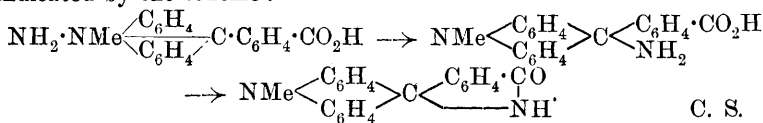
Ammonium Compounds. XXI. Action of Amines on Quaternary Salts of 5-Phenylacridine-o-carboxylic Acid. HERMAN DECKER and CARL SCHENK (*Ber.*, 1906, 39, 748—752. Compare Abstr., 1904, i, 450).—*Ethyl 5-phenylacridine-o-carboxylate* (*acridylbenzoate*), $N \begin{smallmatrix} \diagup C_6H_4 \\ \diagdown C_6H_4 \end{smallmatrix} \cdot C \cdot C_6H_4 \cdot CO_2Et$, is obtained by passing hydro-

gen chloride into an alcoholic solution of the acid at 60—70°; it sublimes in bright yellow needles, melts at 161°, dissolves in dilute acids to a fluorescent solution, and is rapidly hydrolysed by boiling alkalis. The *hydriodide*, $C_{22}H_{17}O_2N \cdot HI$, forms orange needles which melt and decompose at 216°, and separates from water and alcohol with partial decomposition; the *picrate*, $C_{22}H_{17}O_2N \cdot C_6H_3O_7N_3$, separates from alcohol in small, yellow needles which melt at 244°; the *dichromate*, $(C_{22}H_{17}O_2N)_2 \cdot H_2Cr_2O_7 \cdot H_2O$, forms orange needles and melts when anhydrous at 141°. The *methiodide* forms garnet-red needles and melts and decomposes at 220°.

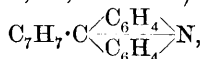
The *lactam* of 5-amino-5-phenyl-10-methyldihydroacridine-*o*-carboxylic acid, $NMe \langle \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} \rangle C \langle \begin{smallmatrix} NH \\ C_6H_4 \end{smallmatrix} \rangle CO$, is obtained together with the lactone by the action of ammonia on the quaternary salts of 5-phenylacridine-*o*-carboxylic acid, its esters, or the betaine compound. The lactam is more soluble in benzene than the lactone, and separates from this solvent in colourless needles which contain benzene of crystallisation, melts at 243°, and does not form fluorescent solutions in dilute acids.

The *methyl lactam*, $C_{22}H_{18}ON_2$, and the *ethyl lactam*, $C_{23}H_{20}ON_2$, are obtained in a similar way by the use of methylamine and ethylamine respectively, and are separated from the accompanying lactone by treatment with a 1—2 per cent. hydrochloric acid or by crystallisation from dilute alcohol, in which the lactams are less soluble; the methyl compound forms colourless needles and melts at 238°; the ethyl lactam also crystallises in colourless needles and melts at 203°.

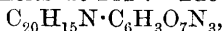
These lactams are not obtained from the lactones by the action of ammonia or amines, and it is suggested that they are derivatives of ammoniumamide, $H_4N \cdot NH_2$, the course of their formation being indicated by the scheme:



Methyl Derivatives of 5-Phenylacridine. ALFRED SCHMID and HERMAN DECKER (*Ber.*, 1906, 39, 933—939).—5-*o*-Tolylacridine,

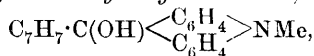


obtained by heating *o*-toluic acid, diphenylamine, and zinc chloride for ten hours at 240—260°, melts at 212°. The *picrate*,

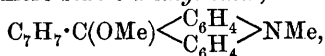


separates from alcohol in yellowish-brown prisms and melts at 226°. The *methiodide* forms dark red needles which melt and decompose at 237°. The *picrate* obtained from the carbinol base or from the quaternary salts melts at 161°.

5-Hydroxy-5-*o*-tolyl-10-methyldihydroacridine,

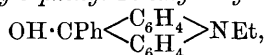


obtained from the quaternary salts by the action of alkalis, is an unstable substance and melts at 149°. By boiling methyl alcohol, it is converted into the more stable *methyl ether*,



which crystallises in colourless prisms and melts at 114° to a red liquid. 5-m-*Tolylacridine*, $\text{C}_{20}\text{H}_{15}\text{N}$, obtained in the same way as its isomeride, forms yellow crystals and melts at 165°. The *picrate* crystallises in small, yellow needles and melts at 253°. The *methiodide* crystallises in dark violet prisms and melts at 232°. The *picrate* obtained from the quaternary salts or from the carbinol base forms long, yellow prisms and melts at 178° and is more soluble than the tertiary *picrate*. The *carbinol* base is quantitatively precipitated by alkalis from solutions of the quaternary salts; it crystallises in colourless prisms, melts at 122°, and slowly turns green in the air. The *methyl ether* melts at 127–128° to a red liquid. The *ethyl ether* forms white needles and melts at 160°.

[With TH. HOCK.]—5-p-*Tolylacridine*, $\text{C}_{20}\text{H}_{15}\text{N}$, forms thick, yellow prisms and melts at 189–190°. The *picrate* melts at 226°, the *methiodide* at 243°, the quaternary *picrate* at 202°, the *carbinol* base at 144°, and its *ethyl ether* at 122° to a red liquid. The last compound shows the iodoform reaction. The *ethiodide* of 5-phenylacridine is obtained in quantitative yield by heating its components at 120° for two hours. It crystallises from water in dark red leaflets and melts at about 223°, evolving ethyl iodide which can be estimated quantitatively (Abstr., 1905, i, 374). The quaternary *picrate*, obtained as well from the ethiodide as from the carbinol base, separates from alcohol in long, yellow needles and melts at 181°. The carbinol base, 5-hydroxy-5-phenyl-10-ethylidihydroacridine,



obtained from the ethiodide by the action of alkalis, crystallises from toluene in colourless cubes and melts at 136–137°. The *ethyl ether*, $\text{C}_{23}\text{H}_{23}\text{ON}$, forms colourless needles and melts at 148° to a red liquid.

p-*Xylene-2-nitrile*, $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{CN}$, obtained from p-xylidine, is a yellow oil, which boils between 223° and 226° under 730 mm. pressure and is difficultly volatile in steam.

5-m-*Xylylacridine*, $\text{C}_{21}\text{H}_{17}\text{N}$, sublimes in yellow needles and melts at 159°. The *picrate* melts at 254°.

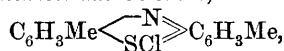
5-p-*Xylylacridine*, $\text{C}_{21}\text{H}_{17}\text{N}$, melts at 176° and the *picrate* at 227°.

C. S.

Constitution of Thiazine and Oxazine Dyes. FRIEDRICH KEHRMANN (Ber., 1906, 39, 914–926).—[With K. MODEBADZÉ.]—

3:9-Dimethylphenothiazine, $\text{C}_6\text{H}_2\text{Me} < \text{NH} > \text{C}_6\text{H}_2\text{Me}$, obtained by rapid distillation of di-p-tolylamine and sulphur, crystallises in greenish-yellow leaflets, melts at 219–220°, does not combine with mineral acids or picric acid, and develops with concentrated sulphuric acid a blood-red colour due to dimethylphenthiazonium sulphate.

3 : 9-Dimethylphenothiazonium chloride,



obtained from the preceding compound by the action of ferric chloride, forms dark green, lustrous needles ; it is soluble in cold water, but the solution, slowly of itself, more rapidly in the presence of sodium acetate, deposits colourless crystals of the ψ -base. The *nitrate* forms sparingly soluble, feathery, red needles.

[With K. MODEBADZÉ and V. VESELY.]—3 : 9-Diacetylaminophenothiazine, $\text{C}_{16}\text{H}_{15}\text{O}_2\text{N}_3\text{S}$, obtained from Lauth's violet by reduction and subsequent acetylation, forms long, colourless needles which melt at 280° , and is insoluble in water or dilute mineral acids.

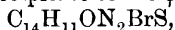
3 : 9-Diacetylaminophenothiazonium chloride,



crystallises from methyl alcohol, slightly acidified with hydrochloric acid, in long, green needles. It is not hydrolysed by cold water ; the addition of sodium acetate only very slowly causes the deposition of a pale yellow ψ -base. Ammonium or sodium carbonate precipitates from the aqueous solution a dark brown, flocculent substance which disappears on boiling and in its place the crystalline ψ -base is obtained. The diacetyl compound is hydrolysed by prolonged boiling of the acidified solution. The *platinichloride*, $(\text{C}_{16}\text{H}_{13}\text{O}_2\text{NS})_2 \cdot \text{H}_2\text{PtCl}_6$, forms violet crystals.

3-Acetylaminophenothiazine forms yellow needles, melts at 208° , and is insoluble in water or dilute mineral acids.

3-Acetylaminophenothiazonium chloride, $\text{C}_6\text{H}_4 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{S} \text{Cl} \end{array} \text{C}_6\text{H}_3 \cdot \text{NHAc}$, is partially hydrolysed by cold water ; the addition of an alkaline carbonate produces a crystalline precipitate of the ψ -base. The *bromide*,



consists of a dark brownish-violet, crystalline powder, sparingly soluble in cold water.

After discussing the properties of 3-anilinophenothiazonium chloride, 3-aminophenothiazonium chloride, Lauth's violet (3 : 9-diaminophenothiazonium chloride), and methylene-blue, the author concludes with a criticism of Hantzsch's views as to the constitution of these thionium compounds (Abstr., 1905, i, 605).

C. S.

4 : 6-Dibromo-*o*-phenylenediamine. C. LORING JACKSON and FREDERICK W. RUSSE (*Amer. Chem. J.*, 1906, **35**, 148—154).—4 : 6-Dibromo-*o*-phenylenediamine, $\text{C}_6\text{H}_2\text{Br}_2(\text{NH}_2)_2$, obtained by reducing 4 : 6-dibromo-2-nitroaniline with tin and hydrochloric acid, crystallises in plates or needles, melts at 83° , darkens on exposure to the air, and is freely soluble in alcohol and slightly so in hot water. The *hydrochloride* forms transparent needles ; the *hydrobromide* crystallises in short prisms. The amine dissolves in strong sulphuric acid and, on dilution, flat, transparent prisms are deposited. The *diacetyl* derivative, $\text{C}_6\text{H}_2\text{Br}_2(\text{NHAc})_2$, crystallises in long, white needles and melts at 227 — 228° .

10 : 12-Dibromophenanthraphenazine (5 : 7-dibromo-2 : 3-diphenylenequinoxaline), $\text{C}_{20}\text{H}_{10}\text{N}_2\text{Br}_2$, obtained by the action of phenanthra-

quinone on 4:6-dibromo-*o*-phenylenediamine, crystallises in slender, yellow needles, melts at 248°, is soluble in hot benzene or chloroform, slightly so in alcohol, ether, or acetone, and is insoluble in light petroleum or water.

5:7-Dibromo-2:3-diphenylquinoxaline, $C_{20}H_{12}N_2Br_2$, obtained by the condensation of the amine with benzil, crystallises from dilute alcohol in long, white needles, melts at 149—150°, and is soluble in the usual organic solvents and insoluble in water.

By the action of tetrabromo-*o*-benzoquinone on the amine, a red, tarry mass was obtained from which no definite compound could be isolated. E. G.

[Basic Dyes from Formyl-*m*-diamines.] ANILINFARBEN- & EXTRACT-FABRIKEN VORM. JOH. R. GEIGY (D.R.-P. 161699. Compare Abstr., 1904, i, 530).—The formyl derivatives of *m*-diamines (Abstr., 1903, i, 522) condense with alkylated *m*-diamines or alkylated *m*-aminophenols when heated at 150—250° with ammonium salts or salts of amines. Orange dyes, suitable for use with a tannin mordant or on leather, are thus obtained. C. H. D.

[3:5-Dichloro-4'-dimethylamino-4-hydroxydiphenylamine.] FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 161665).—The indophenol prepared from 2:6-dichlorophenol and *as*-dimethyl-*p*-phenylenediamine yields on reduction with sodium sulphide 3:5-dichloro 4'-dimethylamino-4-hydroxydiphenylamine,

$$OH \cdot C_6H_2Cl_2 \cdot NH \cdot C_6H_4 \cdot NMe_2,$$

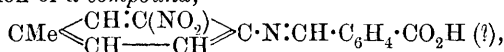
which forms small, white crystals and readily oxidises in air to the indophenol. The preparation may also be carried out without isolating the dichlorophenol by adding 2 mols. of sodium hypochlorite to 1 mol. of sodium phenoxide, adding the calculated quantity of *as*-dimethyl-*p*-phenylenediamine, oxidising, and reducing the indophenol. Blue dyes are obtained on fusing the product with sulphur and sodium sulphide. C. H. D.

Condensation of *o*-Diamines with Phthalonic Acid. CAMILLO MANUELLI and CONCETTO MASELLI (*Gazzetta*, 1905, 35, ii, 572—579. Compare Manuelli and Silvestri, Abstr., 1904, i, 784).—When heated together in alcoholic solution, ethylenediamine and phthalonic acids yield the compound $CH_2 \begin{smallmatrix} < CH_2 - N \\ N : C(OH) \end{smallmatrix} > C \cdot C_6H_4 \cdot CO_2H$, which melts and decomposes at 176°, and, in aqueous solution, decomposes barium and calcium carbonates. The silver salt, $C_{11}H_8O_3N_2Ag_2$, was prepared and analysed.

The condensation of 1-tolylene-3:4-diamine and phthalonic acid in aqueous or alcoholic solution yields 3-hydroxy-6(or 7)-methylquinoxaline-2-benzoic acid, $C_6H_3Me \begin{smallmatrix} < N : C \\ N : C(OH) \end{smallmatrix} > C \cdot C_6H_4 \cdot CO_2H$, which separates as a white, crystalline powder melting and decomposing at 245°. The calcium salt, $(C_{16}H_{11}O_3N_2)_2Ca \cdot 8H_2O$, crystallises in silky needles. The lactone, $C_6H_3Me \begin{smallmatrix} < N : C \\ N : C - O \end{smallmatrix} > CO$, prepared by heating the acid at a

temperature slightly above its melting point, crystallises from benzene in elongated prisms or from alcohol in iridescent scales melting at 225° . On treatment with alcoholic ammonia solution, the lactone is converted into the *imino*-compound, $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{N}:\text{C}\cdot\text{C}_6\text{H}_4 \\ \text{N}:\text{C}-\text{NH} \end{smallmatrix} > \text{CO}$, which separates from alcohol in slender, pale yellow needles melting at 303° ; the *aurichloride*, $\text{C}_{16}\text{H}_{11}\text{ON}_3\cdot\text{HAuCl}_4$, forms pale yellow prisms, and the *platinichloride*, $(\text{C}_{16}\text{H}_{11}\text{ON}_3)_2\cdot\text{H}_2\text{PtCl}_6$, intensely yellow, acicular crystals.

On heating molecular proportions of *m*-nitro-*p*-toluidine and phthalonic acid in alcoholic solution in a sealed tube, condensation takes place with formation of a compound,



which crystallises from benzene in iridescent, yellow needles melting at 198° and dissolves in solutions of the alkali hydroxides or carbonates.

T. H. P.

Piperazine Benzoate and Salicylate. A. ASTRUC (*Bull. Soc. chim.*, 1906, [iii], 35, 169—171. Compare Abstr., 1905, i, 382, 671).—*Piperazine benzoate*, $\text{C}_4\text{H}_{10}\text{N}_2(\text{C}_7\text{H}_6\text{O}_2)_2$, is precipitated when solutions of the acid and of the base in alcohol are mixed. It crystallises in small lamellae, sublimes at 120° , has a faint odour of benzoic acid, dissolves in 4.2 parts of water, in 16.3 parts of alcohol (90 per cent.), and in 46.4 parts of absolute alcohol at 15° , is alkaline to helianthin, and acid to phenolphthalein. In presence of the latter indicator, 1 mol. of potassium hydroxide is required to produce neutrality.

Piperazine salicylate, prepared in the same manner as the benzoate, forms colourless needles, is inodorous, has a sweet taste, and sublimes at 160° . It dissolves in 90 parts of water, in 200 parts of alcohol (90 per cent.), and in 450 parts of absolute alcohol at 15° , is neutral to helianthin, and acid to phenolphthalein. In presence of the latter indicator, 1 mol. of potassium hydroxide is required to produce neutrality. The reactions of the solutions of these salts with solutions of a number of metallic salts are given in the original.

T. A. H.

Trihydroxymethyldihydrouracil. ROBERT BEHREND and HANS OSTEN [with CARL BEER] (*Annalen*, 1905, 343, 133—151).—In order to account for the peculiarities observed in the oxidation of the various methyl- and dimethyl-uracils (Behrend and Grünwald, Abstr., 1902, i, 834), it was thought that trihydroxymethyl- or dimethyl-dihydrouracil was formed as an intermediate product. These substances have now been more minutely investigated.

α-Trihydroxymethyldihydrouracil, $\begin{smallmatrix} (\text{OH})_2\text{C}\cdot\text{CO}\cdot\text{NH} \\ \text{OH}\cdot\text{CMe}-\text{NH} \end{smallmatrix} > \text{CO}$, has been prepared from methyluracil; the latter is first nitrated by treatment with a mixture of nitric acid and phosphoric oxide, the nitrouracil crystallising in prisms or leaflets melting and decomposing at 290° . Aminomethyluracil is obtained by reduction of the nitro-derivative in ammoniacal solution with amalgamated aluminium. When treated

with bromine in suspension in water, the trihydroxy-compound is formed as white crystals melting at 127—128°; the melting point depends on the rate of heating, a temperature of 136° being occasionally observed. When heated at 110°, it loses 2H₂O and is converted into an insoluble powder which decomposes at 140—145° and gives a blue coloration with ferric chloride.

β-Trihydroxymethylidihydrouracil is prepared by dissolving dibromohydroxymethyluracil in potassium hydroxide, neutralising with hydrochloric acid, and then evaporating over sulphuric acid; it forms crystals melting at 116—117°; it is converted into the *α*-derivative by treatment with acids, and is formed from the *α*-isomeride by heating in neutral solution or by very cautious treatment with alkali hydroxides.

With ethyl alcohol, the *α*-compound yields an *α-hydroxydiethoxymethylidihydrouracil*,
$$\begin{array}{c} (\text{OEt})_2\text{C} \cdot \text{CO} \cdot \text{NH} \\ | \\ \text{OH} \quad \text{CMe} \cdot \text{NH} \end{array} > \text{CO},$$
 which forms crystals melting at 180—182°, and is reconverted into the trihydroxy-derivative by water at a low temperature. The *β*-trihydroxy-derivative also yields a *β-hydroxydiethoxymethylidihydrouracil*, which sinters at 105° and melts at 134—136°, and is reconverted into the trihydroxy-compound by water.

The two isomerides also give with phenylhydrazine two distinct compounds; with phenylhydrazine acetate in aqueous solution, the *α*-derivative yields a compound,
$$\text{NH} < \begin{array}{c} \text{CO} \cdot \text{NH} \cdot \text{CO} \\ | \\ \text{CMe}(\text{OH}) \end{array} > \text{C}(\text{OH}) \cdot \text{NH} \cdot \text{NHPh} \quad \text{or}$$

$$\text{CO} < \begin{array}{c} \text{NH} \text{---} \text{CO} \\ | \\ \text{NH} \cdot \text{CMe}(\text{OH}) \end{array} > \text{CO}, \text{NH}_2 \cdot \text{NHPh},$$
 which forms yellow crystals decomposing at 170—180° and behaves as a hydrazide, phenylhydrazine being set free by alkali hydroxides. The *β*-derivative melts at 125° and has similar properties.

When oxidised by permanganate in the presence of potassium hydrogen carbonate, both the uracils yield potassium acetoxalurate, but, in the presence of excess of alkali hydroxide, an oxalate and acetylcarbamide. When the oxidation is carried out by permanganate at a higher temperature, oxaluric acid is formed. The acetallanturic acid, formed by boiling *β*-trihydroxymethylidihydrouracil with water, is oxidised by chromic acid to parabanic acid.

So far, the isomerism of the trihydroxymethylidihydrouracils has not been accounted for. K. J. P. O.

Oxidation of Methylated Methyluracils. ROBERT BEHREND and CARL HUFSCMIDT (*Annalen*, 1905, 343, 155—168).—It was observed (Abstr., 1903, i, 739) that trimethyluracil yielded on oxidation hydroxy-*β*-dimethyluracil,
$$\begin{array}{c} \text{CO} : \text{C}(\text{OH}) : \text{CMe} \\ | \\ \text{NMe} \text{---} \text{CO} \cdot \text{NH} \end{array}.$$
 Since it was possible that this substance was formed from a small quantity of *β*-dimethyluracil present as an impurity in the trimethyluracil, the experiments have been repeated.

Pure trimethyluracil was prepared by methylating *α*-dimethyluracil with methyl iodide and potassium hydroxide; it melted at 111—112°, and was oxidised by a 2 per cent. solution of permanganate in the presence of acetic acid. The hydroxy-*β*-dimethyluracil thus

obtained crystallised in rhombic leaflets decomposing at 335° . On further oxidation, it yielded *s*-acetylmethylcarbamide.

Dimethyluracil yields on oxidation hydroxymethyluracil, and probably also hydroxy- α -dimethyluracil, which is obtained in slender needles melting at 254 — 258° .

β -Dimethyluracil gives on oxidation the hydroxy- β -dimethyluracil previously described; it is coloured deep blue by ferric chloride. Its acetyl derivative was prepared, and was identical with the substance obtained from trimethyluracil.

K. J. P. O.

Nitration of Trimethyluracil. ROBERT BEHREND and CARL HUFSCHMIDT (*Annalen*, 1905, 343, 168—175).—Trimethyluracil was nitrated with a mixture of sulphuric acid and nitric acid saturated with oxides of nitrogen. When the nitration is carried out at as low a temperature as possible, a green substance, $C_7H_6O_4N_4$ or $C_7H_8O_4N_4$, an intermediate product, was obtained; it melted and decomposed at 168° . When reduced with tin and hydrochloric acid at 0° , a sparingly soluble compound, $C_7H_8O_3N_4$, $C_{14}H_{18}O_6N_8$, or $C_7H_{10}O_3N_4$, is formed, which melts and decomposes at 227° and is soluble in, but decomposed by, potassium hydroxide; it can be recrystallised from concentrated hydrochloric or sulphuric acid or acetic acid, from which it separates in dark yellow needles.

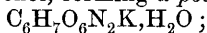
When the reduction is carried out at the ordinary temperature, a readily soluble compound, $C_7H_9O_4N_3$, is produced; it crystallises in long needles melting at 215° ; it is readily soluble in water, acids, and alkali hydroxides, and gives with ferric chloride an intense blue coloration. Its *acetyl* derivative melts at 162 — 172° .

When the trimethyluracil is nitrated at the ordinary temperature, *nitrodimethyluracilcarboxylic acid*, $C_7H_7O_6N_3 \cdot 2H_2O$, which melts and decomposes at 139 — 140° , and nitrodimethyluracil (m. p. 150 — 154°) are formed. The acid is obtained in larger proportion when the mixture is cooled.

K. J. P. O.

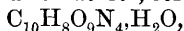
Dialuric Acid. ROBERT BEHREND and HERMANN FRIEDRICH (*Annalen*, 1906, 344, 1—18. Compare Menschutkin, this Journal, 1876, i, 907).—On preparing potassium, sodium, and ammonium dialurates by Menschutkin's methods (*loc. cit.*), the author obtained salts only of the type $C_4H_3O_4N_2M'$. This is in agreement with Koech's results (Abstr., 1901, i, 262), and Menschutkin's supposed salts of the type $C_7H_8O_{10}N_4M'_2$, are considered to be non-existent.

When finely powdered and boiled with acetic anhydride, dialuric acid forms the *acetyl* derivative, $CO \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{CH} \cdot \text{OAc}$, which crystallises in white prisms or leaflets, melts at 210 — 212° , is readily soluble in water or alcohol, but less so in ether, and when recrystallised from boiling water decomposes partially, yielding a product melting and becoming red at 200 — 210° . It forms a violet precipitate with barium hydroxide in aqueous solution, and interacts with potassium acetate in 95 per cent. alcohol, forming a *potassium* salt,



this is obtained as a fine crystalline precipitate, loses H_2O over soda-

lime in a vacuum, melts and decomposes at 300—303°, has an acid reaction in aqueous solution, is not precipitated from its aqueous solution by barium or calcium chloride, but with lead acetate forms a *precipitate* consisting of white leaflets, and reduces cold silver nitrate or ammoniacal silver solutions. Acetyldialuric acid interacts with alloxan in aqueous solution at 40°, forming *acetylalloxantin*,



which crystallises in thin leaflets resembling those of alloxantin, loses H_2O over sulphuric acid in a vacuum, melts and decomposes with ebullition at 263—265°, and is hydrolysed slowly by hot water with formation of alloxantin.

Benzoyldialuric acid, $\text{C}_{11}\text{H}_8\text{O}_5\text{N}_2$, formed by heating dialuric acid with benzoyl chloride at 190—200°, crystallises from alcohol in prisms or leaflets, melts at 209—210°, is readily soluble in alcohol, but less so in ether, and only sparingly so in cold water or benzene, and with barium hydroxide in aqueous solution gives, after some time, a bluish-violet coloration. It interacts with alloxan in hot aqueous solution, forming *benzoylalloxantin*, $\text{C}_{15}\text{H}_{10}\text{O}_9\text{N}_4\cdot\text{H}_2\text{O}$ or $1\frac{1}{2}\text{H}_2\text{O}$, which crystallises from hot water in colourless, hexagonal leaflets, melts at 253—255°, and with barium hydroxide in aqueous solution yields a white precipitate changing to bluish-violet.

If acetylalloxantin is dissolved in pyridine, acetic anhydride added, and the mixture evaporated over sulphuric acid and lime in a vacuum, there is obtained a crystalline *additive* product, $\text{C}_{10}\text{H}_8\text{O}_9\text{N}_4\cdot\text{C}_5\text{H}_5\text{N}$, which dissolves in dilute sodium hydroxide, yielding an odour of pyridine. The action of ammonium carbonate on acetylalloxantin in aqueous solution leads to the formation of murexide (compare Piloty and Finckh, Abstr., 1904, i, 820); contrary to the statement of these authors, murexide crystallises with less than $1\text{H}_2\text{O}$, or loses part of its water of crystallisation when dried in air; at 120°, it commences to decompose with evolution of ammonia.

Quinol diacetate resembles the dialkyl ethers of quinol in that it does not interact with quinone in cold alcohol or ethereal solution; this is of importance in view of the formation of alloxantin from acetyldialuric acid and the parallel drawn by Piloty and Finckh (*loc. cit.*) between the formation of alloxantin and that of quinhedrone.

isoDialuric acid, which contains the grouping $-\text{CH}(\text{OH})\cdot\text{C}(\text{OH})_2-$, does not form a compound resembling alloxantin with alloxan or with dialuric acid. As *isodialuric acid* is easily soluble in water, contains 1 mol. of water of constitution, and interacts readily with hydroxylamine hydrochloride forming an oxime, it has most probably the molecular formula $\text{C}_4\text{H}_6\text{O}_4\text{N}_2$, and is not itself a compound of the nature of alloxantin (compare Behrend and Roosen, Abstr., 1888, 581).

G. Y.

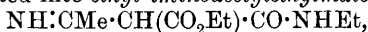
Action of Thiocarbimides on Ethyl Aminocrotonate. ROBERT BEHREND and HANS HENNICKE (*Annalen*, 1906, 344, 19—29. Compare Behrend, Meyer, and Buchholtz, Abstr., 1901, i, 136; Behrend and Hesse, Abstr., 1904, i, 379).—*Ethyl iminoacetyl-p-tolylthiomalonamate*, $\text{NH}\cdot\text{CMe}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$, or *ethyl aminoethylidene-p-tolylthiomalonamate*, $\text{NH}_2\cdot\text{CMe}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$, is formed by

the interaction of *p*-tolylthiocarbimide with ethyl aminocrotonate during some weeks at the laboratory temperature, or, together with small amounts of thion-*p*-tolylmethyluracil, more quickly on the water-bath; it crystallises from alcohol in yellow, prismatic needles, melts at 125—130°, and is moderately soluble in alcohol or benzene, but is almost insoluble in water or ether.

Thion-p-tolylmethyluracil, $\text{CS} \begin{smallmatrix} \text{NH} - \text{CMe} \\ \text{N}(\text{C}_7\text{H}_7) \cdot \text{CO} \end{smallmatrix} \text{CH}$, crystallises in slender, almost colourless needles, melts at 278—279°, and is soluble in dilute sodium hydroxide.

The action of allylthiocarbimide on ethyl aminocrotonate for five weeks at the laboratory temperature, or for four to five hours at 70°, leads to the formation of *ethyl iminoacetylallylthiomalonamate*, $\text{C}_{10}\text{H}_{16}\text{O}_2\text{N}_2\text{S}$, which crystallises from 95 per cent. alcohol in snow-white, slender needles and melts at 105—106°. No thionmethylallyluracil is formed.

Ethyl iminoacetyl ethylthiomalonamate, $\text{C}_9\text{H}_{16}\text{O}_2\text{N}_2\text{S}$, but no thion-methylethyluracil, is formed by the interaction of ethylthiocarbimide and ethyl aminocrotonate for two months at the laboratory temperature; the ester crystallises from alcohol in snow-white needles and melts at 130—131°. When digested with silver carbonate and alcohol, the ester is converted into *ethyl iminoacetyl ethylmalonamate*,

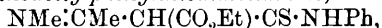


which separates from light petroleum in matted, slender needles or, on exposure to air, in transparent, compact crystals containing H_2O .

Benzylthiocarbimide, boiling at 140—141° under 17 mm. pressure, is obtained in a yield of 23 per cent. of the theoretical by distilling benzyl thiocyanate four times under the atmospheric pressure and fractionating the product in a vacuum. With ethyl aminocrotonate, it forms *ethyl iminoacetylbenzylthiomalonamate*, $\text{C}_{14}\text{H}_{18}\text{O}_2\text{N}_2\text{S}$, slowly at the laboratory temperature, more quickly at 70°; the ester separates from alcohol in large, greenish-yellow crystals and melts at 115—116°.

The action of phenylthiocarbimide on methyl aminocrotonate leads to the formation, slowly at the laboratory temperature, more quickly on the water-bath, of methyl iminoacetylphenylthiomalonamate, or at 130—140° to the formation of thionphenylmethyluracil, melting at 253—254°. The *ester*, $\text{NH}:\text{CMe} \cdot \text{CH}(\text{CO}_2\text{Me}) \cdot \text{CS} \cdot \text{NHPh}$, separates from alcohol in light yellow crystals, melts at 153—154°, and is slightly soluble in dilute sodium hydroxide.

Ethyl methyliminoacetylphenylthiomalonamate,



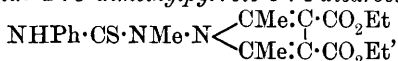
formed by the action of phenylthiocarbimide on ethyl methylaminocrotonate, separates from alcohol in transparent, dark yellow crystals and melts at 107—108°.

The action of phenylthiocarbimide on ethyl β -amino- α -methylcrotonate leads to the formation of thionphenyldimethyluracil and a *product* which separates from alcohol in colourless crystals, melts at 154—155°, and is soluble in aqueous alkali hydroxides. *Thionphenyldimethyluracil*, $\text{NPh} \begin{smallmatrix} \text{CO} \cdot \text{CMe} \\ \text{CS} - \text{NH} \end{smallmatrix} \text{CMe}$, crystallises in slender needles and melts at 254—255°.

Thiontrimethyluracil, $\text{NMe} \begin{smallmatrix} \text{CO} \cdot \text{CMe} \\ \text{CS} - \text{NH} \end{smallmatrix} \text{CMe}$, formed from methylthiocarbimide and ethyl β -amino- α -methylcrotonate at 70—80°, crystallises in snow-white, slender needles and melts at 255—256°. G. Y.

Hydroxyphenylrosindulines. KALLE & Co. (D.R.-P. 160789 and 160815. Compare Abstr., 1905, i, 554, 840).—*p*-Aminophenol condenses with either benzeneazomonoaryl- α -naphthylamines or monoaryl-1:4-diaminonaphthalenes on fusion or on boiling in a reflux apparatus with alcohol or water. The products obtained are bluer in colour than those derived from non-arylated compounds, and probably contain only two hydroxyl groups. C. H. D.

Ethyl 1-Phenylthiouramino-2:5-dimethylpyrrole-3:4-dicarboxylate. CARL BÜLOW and CONSTANTIN SAUTERMEISTER (*Ber.*, 1906, 39, 647—651. Compare Abstr., 1904, i, 690; Bülow and Krafft, Abstr., 1903, i, 196; Bülow, Riess, and Sautermeister, Abstr., 1905, i, 660).—*Ethyl 1-phenylthiocarbamido-2:5-dimethylpyrrole-3:4-dicarboxylate*, $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{N} \begin{smallmatrix} \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \\ \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$, is formed by boiling (1) ethyl 1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate with phenylthiocarbimide or (2) 4-phenylthiosemicarbazide with ethyl diacetylsuccinate in alcoholic solution in a reflux apparatus. It crystallises in glistening, white, rhombic needles, melts at 197°, is readily soluble in alcohol, ether, benzene, pyridine, aqueous ammonia, or dilute alkali hydroxide, and is precipitated from its alkaline solutions on acidification with acetic acid. When treated with methyl sulphate in ice-cooled, aqueous potassium hydroxide solution, it forms *ethyl 1- β -phenylmethylthiocarbamido-2:5-dimethylpyrrole-3:4-dicarboxylate*,



which crystallises from alcohol in needles and melts at 154°, together with a small quantity of a substance which is precipitated from the mother liquors by carbon dioxide or acetic acid, and melts at 80—90°, or, after three recrystallisations from alcohol, at 214—215°.

When shaken with benzoyl chloride and aqueous potassium hydroxide, ethyl 1-phenylthiocarbamidodimethylpyrroledicarboxylate yields ethyl 1-benzoylamino-2:5-dimethylpyrrole-3:4-dicarboxylate, melting at 124°.

Hydrazodicarbonanilide, formed by the action of phenylcarbimide on 4-phenylthiosemicarbazide in warm alcoholic solution, crystallises in delicate, glistening, white leaflets and melts at 212—213°. Curtius and Burkhardt, who prepared this substance by the action of iodine or of heat on phenylsemicarbazide, found it to crystallise in prisms and melt at 245° (Abstr., 1899, i, 137). G. Y.

Reduction in the Diphenylmethane Series. HENRI DUVAL (*Compt. rend.*, 1906, 142, 341—342. Compare Abstr., 1905, i, 651).—2:2':4:4'-*Tetraminodiphenylmethane*, obtained when 4:4'-diamino-2:2'-azodiphenylmethane is reduced with stannous chloride in hydro-

chloric acid solution, forms colourless crystals, soluble in alcohol or water, insoluble in ether, and yields a *dibenzoyl* derivative melting at 275°, which is sparingly soluble in alcohol and insoluble in water. When 4:4'-diamino-2:2'-azodiphenylmethane is reduced by zinc dust in alkaline solution, 4:4'-diaminoacridine is produced; this forms yellow needles melting at 284° (Schöpf gives 281°, Abstr., 1894, i, 598).
M. A. W.

Oxidation Products of Thiocarbamides and their Isomerides.

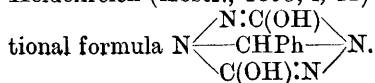
K. DOST (*Ber.*, 1906, **39**, 863—866. Compare Hector, Abstr., 1889, 872).—When the product, obtained by the oxidation of phenylthiocarbamide with hydrogen peroxide, is boiled gently with fuming hydrochloric acid for 3·5 hours, it is converted into a *compound*, $C_{14}H_{11}ON_3S$, which crystallises from alcohol in long, glistening needles melting at 162°. The compound does not form salts and is not acetylated when boiled with acetic anhydride. It has not been found possible to replace a second NH group in the oxidation product by oxygen, and the formula $NH \begin{smallmatrix} \diagup C(NH) \cdot NPh \\ \diagdown C(NPh) \cdot S \end{smallmatrix}$ is suggested instead of Hector's formula $NPh \begin{smallmatrix} \diagup C(NH) \cdot NPh \\ \diagdown C(NH) \cdot S \end{smallmatrix}$. The oxygen compound is then $NH \begin{smallmatrix} \diagup CO \text{---} NPh \\ \diagdown C(NPh) \cdot S \end{smallmatrix}$. The oxidation product of *p*-tolylthiocarbamide, when treated in a similar manner, yields a *product*, $C_{16}H_{15}ON_3S$, melting at 163°.

The two oxidation products are readily transformed into isomerides when heated with alcoholic ammonia at 145—150° for 2·25 hours. The derivative from the oxidation product of phenylcarbamide melts at 198° and the homologue at 203°. Both compounds have lost their basic properties. The phenyl derivative yields an *acetyl* compound, $C_{14}H_{11}N_4SAc$, which melts at 235°. The *p*-tolyl derivative combines with phenylcarbimide, yielding a *compound* $C_{14}H_{12}N_4S, 2CONPh$, melting at 168°.
J. J. S.

Condensation of Aldehydes with *s*-Dihydropyrazines.

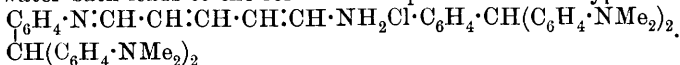
ROBERT STOLLÉ (*Ber.*, 1906, **39**, 826—827. Compare Abstr., 1903, i, 721; 1905, i, 249; also Ruhemann and Merriman, *Trans.*, 1905, 87, 1768).—It has been shown previously that diphenyl-*s*-dihydropyrazine condenses with benzaldehyde and, since a molecular rearrangement, as suggested by Ruhemann and Merriman, is impossible in this case, the original constitutional formulæ are regarded as established.

The benzylidene derivative of dicarbamide described by Curtius and Heidenreich (Abstr., 1895, i, 12) is regarded as having the constitu-



J. J. S.

Influence of Methyl Groups on the Shade of Dyes containing Two Triphenylmethane Groups joined by a Glutaconic Aldehyde Group. FRITZ REIZENSTEIN and JULIUS ROTHSCILD (*J. pr. Chem.*, 1906, [ii], 73, 192—206. Compare Reizenstein and Runge, *Abstr.*, 1905, i, 300; Zincke, Heuser, and Möller, *Abstr.*, 1904, i, 921).—The action of dinitrophenylpyridinium chloride on aminotetramethyldiaminotriphenylmethanes in alcoholic solution on the water-bath leads to the formation of products of the type



When oxidised with lead peroxide in acetic acid, these substances form solutions which dye purer and more intense shades than the corresponding triphenylmethane dyes; as compared with each other, those containing methyl groups in the ortho-position give weaker colours.

The *hydrochloride* $\text{C}_{53}\text{H}_{61}\text{N}_6\text{Cl}$, formed from 4-amino-4':4''-tetramethyldiamino-3-methyltriphenylmethane, is obtained as a red powder melting at about 95° ; the *dye* colours cotton-wool, mordanted with tannin, dark blue.

The *hydrochloride* $\text{C}_{53}\text{H}_{61}\text{N}_6\text{Cl}$, obtained from 4-amino-4':4''-tetramethyldiamino-2-methyltriphenylmethane, is yellowish-green and melts at about 95° ; the *dye* colours cotton-wool, mordanted with tannin, dark corn-flower blue.

The *hydrochloride* $\text{C}_{53}\text{H}_{61}\text{N}_6\text{Cl}$, formed from 2-amino-4':4''-tetramethyldiamino-5-methyltriphenylmethane, is yellowish-brown, sinters at 75° , and melts at about 95° . The corresponding *ammonium hydroxide*, $\text{C}_{53}\text{H}_{61}\text{N}_6\cdot\text{OH}$, is a reddish-brown powder melting at about 81° . The *dye* colours cotton-wool, mordanted with tannin and potassium hydrogen tartrate, indigo-blue.

The *hydrochloride* $\text{C}_{53}\text{H}_{61}\text{N}_6\text{Cl}$, formed from 3-amino-4':4''-tetramethyldiamino-4-methyltriphenylmethane, is greenish-yellow and melts at 78° . The *dye* colours mordanted cotton-wool intense green.

The *hydrochloride* $\text{C}_{53}\text{H}_{61}\text{N}_6\text{Cl}$, formed from 3-amino-4':4''-tetramethyldiamino-5-methyltriphenylmethane, is dark red, sinters at 102° , and melts at 115° . The *dye* colours cotton-wool, mordanted with tannin, dark greenish-blue.

The *hydrochloride* $\text{C}_{53}\text{H}_{61}\text{N}_6\text{Cl}$, formed from 3-amino-4':4''-tetramethyldiamino-6-methyltriphenylmethane, is obtained as a red powder melting at about 130° . The *dye* colours cotton-wool, mordanted with tannin, bluish-green.

The *hydrochloride* $\text{C}_{57}\text{H}_{69}\text{N}_6\text{Cl}$, formed from 4-amino-4':4''-tetramethyldiamino-2':2'':3-trimethyltriphenylmethane, is brownish-yellow, sinters at 90° , and melts at 115° . The *dye* is a weak bluish-green.

The *hydrochloride* $\text{C}_{57}\text{H}_{69}\text{N}_6\text{Cl}$, formed from 4-amino-4':4''-tetramethyldiamino-2:2':2'-trimethyltriphenylmethane, is yellowish-brown, sinters at 90° , and melts at 109° . The *dye* colours cotton-wool, mordanted with tannin, a weak green.

The *hydrochloride* $\text{C}_{57}\text{H}_{69}\text{N}_6\text{Cl}$, formed from 2-amino-4':4''-tetramethyldiamino-2':2'':5-trimethyltriphenylmethane, is a dark brown powder which sinters at 90° and melts at 112° . The *dye* colours cotton-wool, mordanted with tannin, a weak green.

The preceding three derivatives of trimethyltriphenylmethane dissolve in glacial acetic acid forming intensely green solutions. No diminution in the intensity consequent on the introduction of methyl groups the *o*-position can be observed. This applies also to the following three condensation products.

The *hydrochloride* $C_{57}H_{69}N_6Cl$, formed from 3-amino-4':4''-tetramethyldiamino-2':2'':4-trimethyltriphenylmethane, is dark yellow, sinters at 85° , and melts at 115° . The *dye* colours cotton-wool, mordanted with tannin, a weak light green.

The yellowish-brown *hydrochloride*, $C_{57}H_{69}N_6Cl$, formed from 3-amino-4':4''-tetramethyldiamino-2':2'':5-trimethyltriphenylmethane, sinters at 85° and melts at 113° . The *dye* colours cotton-wool, mordanted with tannin, a weak light green.

The brown *hydrochloride*, $C_{57}H_{69}N_6Cl$, formed from 3-amino-4':4''-tetramethyldiamino-2':2'':6-trimethyltriphenylmethane, sinters at 105° and melts at 115° . The *dye* colours cotton-wool, mordanted with tannin, a weak light green.

The red *hydrochloride*, $C_{51}H_{57}N_6Cl$, formed from *o*-aminoleucomalachite-green, sinters at 40° and melts at 68° . The *dye* colours cotton-wool, mordanted with tannin, bluish-green.

The green *hydrochloride*, $C_{51}H_{57}N_6Cl$, formed from *m*-aminoleucomalachite-green, melts at 78° . The *dye* colours cotton-wool, mordanted with tannin, intense emerald-green.

The green *hydrochloride*, $C_{51}H_{57}N_6Cl$, formed from *p*-aminoleucomalachite-green, melts at about 72° . The *dye* colours cotton-wool, mordanted with tannin, dark blue.

The dark yellowish-brown *hydrochloride*, $C_{55}H_{65}N_6Cl$, formed from 2-amino-4':4'-tetramethyldiamino-2':2''-dimethyltriphenylmethane, melts at 102° . The *dye* colours cotton-wool, mordanted with tannin, a weak bluish-green.

The yellowish-brown *hydrochloride*, $C_{55}H_{65}N_6Cl$, formed from 3-amino-4':4''-tetramethyldiamino-2':2''-dimethyltriphenylmethane, melts at about 82° . The *dye* colours cotton-wool, mordanted with tannin, yellowish-green.

The yellow *hydrochloride*, $C_{55}H_{65}N_6Cl$, formed from 4-amino-4':4''-tetramethyldiamino-2':2''-dimethyltriphenylmethane, sinters at 60° and melts at 78° . The *dye* colours cotton-wool, mordanted with tannin and potassium hydrogen tartrate, lilac.

2-Chloro- and 4-chloro-pyridine dissolve in 1-chloro-2:4-dinitrobenzene, forming a yellow solution which becomes dirty brown when heated at 190 — 200° and a red solution which solidifies to a yellowish-red mass respectively. In neither case does any interaction take place, as the constituents of the mixtures can be separated by treatment of the products with ether.

G. Y.

Liquid-crystalline Substances. [Azoxy-compounds.] DANIEL VORLANDER (*Ber.*, 1906, 39, 803—810. Compare Vorländer and Meyer, *Abstr.*, 1902, i, 328; Meyer and Dallem, *Abstr.*, 1903, i, 448).—It is found that in general the formation of an anisotropic liquid is conditioned by the presence of atomic groups which influence other

physical properties, such as the refractivity, the colour, or the specific rotation.

Whilst ethyl *p*-azoxybenzoate exists between 114° and 121° as liquid crystals, the following esters of *p*-azoxybenzoic acid do not form anisotropic liquids; the temperatures given are the melting points :

Methyl, 203°; *n-propyl*, 103°; *isopropyl*, 96°; *n-butyl*, 105°; *isoamyl*, 122°; *allyl*, 88—89°; *benzyl*, 147°.

p-Azoxycinnamic acid is prepared by reducing *p*-nitrocinnamic acid with arsenious oxide in aqueous sodium hydroxide solution; its esters, which are prepared by the action of the alkyl iodide or bromide on the dry silver salt, crystallise mostly in golden-yellow needles, the *n*-propyl ester in prismatic plates, and give an orange-red coloration with concentrated sulphuric acid. The following aliphatic esters of *p*-azoxycinnamic acid form liquid crystals; the temperatures given are the first and second melting points between which the anisotropic liquid exists :

Methyl, 219—221°, 254—257°; *ethyl*, 141°, 247—249°; *n-propyl*, 123°, 240—243°; *isopropyl*, 148—150°, 184°; *n-butyl*, 110—111°, 214°; *isoamyl*, 144°, 184—186°; *n-octyl*, 94°, 175°; *cetyl*, 105°, 139—141°; *allyl*, 124°, 234—237°; *carbethoxymethyl*, $\text{OEt} \cdot \text{CO} \cdot \text{CH}_2$, 146—148°, 233—235°; *phenacyl*, 229—231°, 238°.

Benzyl p-azoxycinnamate melts directly to the isotropic liquid at 174—175°.

The colourless *tetrabromide*, obtained by the action of bromine on ethyl *p*-ethoxycinnamate, melts without passing through an anisotropic phase at 162°.

p-Azoxybenzylidenacetophenone, $\text{C}_{30}\text{H}_{22}\text{O}_3\text{N}_2$, is prepared by reduction of *p*-nitrobenzylidenacetophenone with arsenious oxide in aqueous sodium hydroxide solution; it crystallises in small, pointed, orange-yellow leaflets, gives a blood-red colour with concentrated sulphuric acid, and melts to an anisotropic liquid at 211°, changing to the isotropic phase at 213°.

Di-p-acetoxybenzylidenehydrazone crystallises in small, yellow plates and melts at 185° and again at 192°. The *p*-benzoxy-derivative crystallises in small, yellow needles or plates and melts at 227° and again about 290°.

The *benzenesulphonyl* and *carbethoxy*-derivatives of di-*p*-hydroxybenzylidenehydrazone melt at 167° and 170° respectively and do not form liquid crystals.

Di-*o*-hydroxybenzylidenehydrazone and its methyl and acetyl derivatives and the corresponding *m*-compounds do not form liquid crystals. Whilst dianisylidenehydrazone passes through an anisotropic liquid phase, the hydrazones of piperonal, vanillin, acetyl-vanillin, and veratraldehyde and of derivatives of anisaldehyde in which the *p*-methoxy-group is substituted by an amino-, a dimethyl-amino-, or a nitro-group, when heated melt directly to the isotropic liquid. Under special conditions, the formation of an anisotropic liquid by di-*p*-aminobenzylidenehydrazone and by acetyl-*p*-coumaric acid has been observed.

p-Methoxycinnamic acid, but not its methyl or ethyl ester, forms an anisotropic liquid.

G. Y.

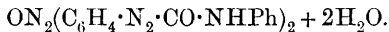
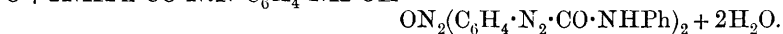
***o*-Azoacetanilide.** STEFAN VON NIEMENTOWSKI (*Ber.*, 1906, **39**, 742—744).—The substance, obtained by the author in 1896 by the reduction of *o*-nitroacetanilide with zinc dust and acetic acid, and regarded by him as oxy- β -methylbenziminazole, agrees in all its properties except crystalline form with *o*-azoacetanilide (compare Willstätter and Pfannenstiel, *Abstr.*, 1905, i, 723); the single difference is probably due to the use of different solvents. C. S.

Action of Sodium Hypobromite on Primary Aromatic Amines. WILHELM MEIGEN and E. NOTTEBOHM (*Ber.*, 1906, **39**, 744—747. Compare *Abstr.*, 1900, i, 702).—The behaviour of sodium hypobromite is similar to that of the hypochlorite. ψ -Cumidine is oxidised to azo- ψ -cumene and *p*-aminobenzoic acid to *p*-azobenzoic acid. 5-Aminoquinoline or bromo-5-aminoquinoline (Claus and Schnell, *Abstr.*, 1896, i, 319) is oxidised to *quinolineazine*, $C_{18}H_{10}N_4$, which crystallises in glassy, yellow needles and melts above 420° ; the *platini-chloride*, $C_{18}H_{10}N_4 \cdot H_2PtCl_6$, forms bronze-yellow crystals. The azine is reduced by stannous chloride and hydrochloric acid to a hydrazine, which forms a dark green double salt with stannous chloride and is reconverted into the azine by atmospheric oxygen or warm dilute nitric acid. C. S.

The Relation between Quinonehydrazones and *p*-Hydroxy-azo-compounds. III. **Quinoneoximehydrazones.** WALTHER BORSCHÉ (*Annalen*, 1905, **343**, 176—207. Compare *Abstr.*, 1905, i, 719).—The hitherto unknown quinoneoximehydrazones are of interest, since they may exhibit a tautomerism with the azo-derivatives of β -phenylhydroxylamine similar to that observed between the quinonehydrazones and the *p*-hydroxyazo-compounds. Since the quinonoid mono-condensation products from quinones and primary hydrazones are not known, the condensation of hydrazines and quinoneoximes is used as a method of preparation. Alkylated hydrazines will not condense with the quinone-oximes, but acylated hydrazines of the types



and $NH_2 \cdot NR \cdot COR$ readily combine with quinoneoximes, yielding the oximehydrazones. The products obtained show very different behaviour with respect to their solubility in alkali hydroxides. Alkaline solutions of some of these compounds are readily oxidised by the air, thus :



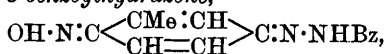
[With H. KÜHL.]—*Quinoneoximebenzoylhydrazone*,



prepared from benzoquinoneoxime and benzoylhydrazine hydrochloride in dilute alcoholic solution, crystallises in brownish-yellow leaflets melting and decomposing at $209-210^\circ$, and is very stable towards alkalis, but oxidised by alkaline oxidising agents; it does not react with hydroxylamine hydrochloride, but is resolved by hydrochloric acid into benzoic acid and *p*-aminophenol, and by sulphuric acid into benzoic acid and phenol; nitric acid converts it into nitrobenzene.

Benzoylbenzoquinoneoximebenzoylhydrazone, $OBz \cdot N : C_6H_4 : N \cdot NHBz$, prepared from benzoylbenzoquinoneoxime and benzoylhydrazine hydrochloride, is a golden-yellow, crystalline powder, melting and decom-

posing at 196—198°, and is soluble in alcoholic alkali hydroxides.
2-Toluquinoneoxime-5-benzoylhydrazine,

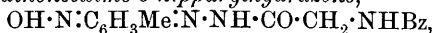


prepared from nitroso-*m*-cresol and benzoylhydrazine hydrochloride, is a yellowish-brown, crystalline powder decomposing at 200—202°. *2-Benzoylthymoquinone-5-benzoylhydrazine*, prepared from benzoylthymoquinoneoxime and benzoylhydrazine hydrochloride, crystallises in yellowish-white needles melting at 236°. *Benzoyl- α -naphthaquinoneoximebenzoylhydrazine*, $\text{OBz}\cdot\text{N}:\text{C}_{10}\text{H}_6:\text{N}\cdot\text{NHBz}$, prepared from benzoyl- α -naphthaquinoneoxime and benzoylhydrazine hydrochloride, crystallises in yellow needles decomposing at 207—208°.

Benzoquinoneoximehippurylhydrazine,

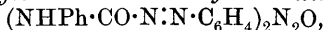


prepared from benzoquinoneoxime and hippurylhydrazine hydrochloride, is a yellowish-white, crystalline powder, melting and decomposing at 219°. *3-Toluquinoneoxime-6-hippurylhydrazine*,



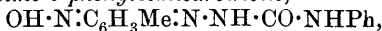
obtained in a similar manner from nitroso-*o*-cresol, is a brown powder at 209°. *2-Toluquinoneoxime-5-hippurylhydrazine*, similarly prepared from nitroso-*m*-cresol, crystallises in brown scales melting and decomposing at 212°. *2-Thymoquinoneoxime-5-hippurylhydrazine* is obtained in a similar manner from 2-thymoquinoneoxime, and crystallises in slender, yellow needles decomposing at 240°. *α -Naphthaquinoneoximehippurylhydrazine*, $\text{OH}\cdot\text{N}:\text{C}_{10}\text{H}_6:\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NHBz}$, prepared from α -naphthaquinoneoxime, is a yellow powder melting at about 260°.

Quinoneoximephenylsemicarbazone, $\text{OH}\cdot\text{N}:\text{C}_6\text{H}_4:\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$, prepared from phenylsemicarbazide hydrochloride and benzoquinoneoxime, crystallises in yellowish-white needles exploding at 217°, and is soluble in alkalis with a reddish-brown coloration. Its *benzoyl* derivative, prepared by benzoylating the hydrazone in pyridine solution, crystallises in insoluble, yellow needles. When air is passed through, or hydrogen peroxide added to the alkaline solution of the hydrazone just mentioned, *azoxybenzene-4 : 4'-disazoformanilide*,

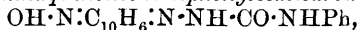


is produced, crystallising in orange-red needles melting and decomposing at 229—230°.

2-Toluquinoneoxime-6-phenylsemicarbazone,



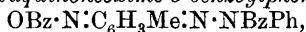
prepared from nitroso-*o*-cresol and phenylsemicarbazide hydrochloride, is a brown, crystalline powder decomposing at about 225°. *2-Toluquinoneoxime-5-phenylsemicarbazone*, prepared from nitroso-*m*-cresol, is a yellow powder exploding at 228—229°. *2-Thymoquinoneoxime-5-phenylsemicarbazone*, $\text{OH}\cdot\text{N}:\text{C}_6\text{H}_2\text{MePr}^s:\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$, prepared from nitrosothymol, crystallises in yellow needles melting at 234°, and insoluble in dilute alkali hydroxides. *3-Thymoquinoneoxime-6-phenylsemicarbazone*, prepared from nitrosocarvacrol, crystallises in yellow needles melting at 204—205° and is insoluble in dilute alkali hydroxides. *α -Naphthaquinoneoximephenylsemicarbazone*,



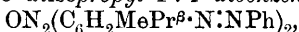
forms yellow crystals melting at 242° ; it is readily soluble in dilute alkali hydroxides, the solution being oxidised neither by air nor by hydrogen peroxide.

Benzoquinoneoximebenzoylphenylhydrazone, $\text{OH}\cdot\text{N}:\text{C}_6\text{H}_4:\text{N}\cdot\text{NPhBz}$, crystallises in yellowish-green rhombohedra or leaflets melting at 177° and soluble in alkali hydroxides; its alkaline solution is oxidised by the air, *dibenzeneazoazoxybenzene*, $\text{ON}_2(\text{C}_6\text{H}_4\cdot\text{N}:\text{NPh})_2$, separating; the latter, which is produced by boiling nitroazobenzene with a sodium methoxide solution, crystallises in orange-yellow needles melting at 218° . On reduction with zinc dust and acetic acid, the benzoquinone-oximebenzoylphenylhydrazone is converted into benzanilide and *p*-phenylenediamine, and when boiled with hydroxylamine hydrochloride in alcoholic solution it yields the dioxime of benzoquinone, and with nitric acid in acetic acid solution *p*-nitroazobenzene.

Benzoylbenzoquinoneoximebenzoylphenylhydrazone, prepared in a similar manner from benzoylbenzoquinoneoxime, crystallises in orange-red leaflets melting at 187 – 188° , and when warmed with alcoholic potassium hydroxide is converted into dibenzeneazoazoxybenzene. *2-Benzoyltoluoquinoneoxime-5-benzoylphenylhydrazone*,



occurs in two forms, which are probably stereoisomeric; one crystallises in red needles melting at 190° and the other in leaflets melting at 202° . When warmed with alcoholic potassium hydroxide, it yields *2:2'-dimethyl-4:4'-dibenzeneazoazoxybenzene*, $\text{ON}_2(\text{C}_6\text{H}_3\text{Me}\cdot\text{N}:\text{NPh})_2$, crystallising in brown needles melting at 158° . *2-Benzoylthymoquinoneoxime-5-benzoylphenylhydrazone*, $\text{OBz}\cdot\text{N}:\text{C}_6\text{H}_2\text{MePr}^i:\text{N}\cdot\text{NBzPh}$, prepared from benzoylnitrosothymol, crystallises in orange-yellow leaflets melting at 183° and is converted by boiling with alcoholic potassium hydroxide into *2:2'-dimethyl-5:5'-diisopropyl-4:4'-dibenzeneazoazoxybenzene*,



which crystallises in dark red needles melting at 147° . K. J. P. O.

Action of Diazohydrates on Oximino-compounds. H. W. BRESLER, W. H. FRIEDEMANN, and JULIUS MAI (*Ber.*, 1906, **39**, 876–883. Compare Abstr., 1892, 163, 1079; Bamberger, Abstr., 1899, i, 589).—*m-Tolylldiazobisacetoxime*, $\text{C}_{13}\text{H}_{20}\text{O}_2\text{N}_4$, prepared by adding the diazo-solution, obtained from *m*-toluidine, hydrochloric acid, and sodium nitrite, to a solution of acetoxime in aqueous sodium hydroxide, separates from ethyl alcohol in yellow needles and melts at 125° . Its alcoholic solution gives a blue coloration with ferric chloride.

o-Tolylldiazobisacetoxime, $\text{C}_{13}\text{H}_{20}\text{O}_2\text{N}_4$, prepared in an analogous manner, separates from ether in yellow needles and melts at 89° . It gives a greenish-blue coloration with ferric chloride.

p-Xyllyldiazobisacetoxime, $\text{C}_{14}\text{H}_{22}\text{O}_2\text{N}_4$, prepared from acetoxime and diazo-*p*-xylene hydroxide, separates from light petroleum in yellow needles and melts at 99° . Its alcoholic solution gives a bluish-green coloration with ferric chloride.

m-Xyllyl-4-diazobisacetoxime, $\text{C}_{14}\text{H}_{22}\text{O}_2\text{N}_4$, prepared from *m*-4-xylidine

in an analogous manner, separates from a mixture of alcohol and ether in pink leaflets and melts at 87°.

The compound $C_{15}H_{24}O_2N_4$, prepared from ψ -cumidine, separates from light petroleum in glistening needles and melts at 98°.

Anisyl-4-diazobisacetoxime, $C_{13}H_{20}O_3N_4$, prepared from *p*-anisidine, separates from methyl alcohol in glistening, nacreous crystals and melts at 125°. With ferric chloride, it forms a greenish-blue coloration, which quickly becomes violet.

Phenetyl-4-diazobisacetoxime, $C_{14}H_{22}O_3N_4$, prepared from *p*-phenetidine, melts at 125—127°.

The compound $C_{15}H_{18}O_4N_4$, prepared from *p*-aminobenzoic acid, is a yellowish-white solid; its silver salt is yellow.

Phenyldiazobismethylethylketoxime, $C_{14}H_{22}O_2N_4$, prepared by the addition of a diazotised aniline solution to methylethylketoxime, separates from 75 per cent. alcohol and melts at 95°. Its alcoholic solution gives a bluish-green coloration with ferric chloride.

p-Nitrodiazobenzeneimide, $C_6H_4O_2N_4$, prepared from methyl ethyl ketoxime and diazotised *p*-nitroaniline, separates from aqueous methyl alcohol in glistening leaflets and melts at 71°.

Phenyldiazobisdiethylketoxime, $C_{16}H_{26}O_2N_4$, prepared from diazobenzene chloride and diethylketoxime, separates from aqueous methyl alcohol in glistening crystals and melts at 55°. With ferric chloride it gives a greenish-blue coloration, which quickly becomes green.

The compound $C_{13}H_{20}O_2N_4$, prepared from propaldoxime and *p*-diazotoluene hydroxide, separates from light petroleum in colourless crystals and melts at 74°.

Benzenediazobis-4-dimethylaminobenzaldoxime, $C_{24}H_{28}O_2N_6$, prepared from diazobenzene hydroxide and *p*-dimethylaminobenzaldoxime, separates from a mixture of chloroform and methyl alcohol in yellow needles and melts at 183—185°.

p-Toluenediazobis-4-dimethylaminobenzaldoxime, $C_{25}H_{30}O_2N_6$, prepared from diazotised *p*-toluidine and *p*-dimethylaminobenzaldoxime, separates from a mixture of chloroform and methyl alcohol in yellow needles and melts at 167°.

Anisole-4-diazobis-4-dimethylaminobenzaldoxime, $C_{25}H_{30}O_3N_6$, prepared from diazotised *p*-anisidine and *p*-dimethylaminobenzaldoxime, crystallises from benzene in yellow needles and melts at 162°.

The introduction of positive groups into the oximes used induces the combination with diazohydroxides to take place more readily. Negative groups have the opposite effect. Stable compounds were obtained only with the lower members of homologous series.

A. McK.

[Azo-dyes from 3:4:6-Trichloroaniline.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 161922. Compare this vol., i, 121).—The diazonium compound of 3:4:6-trichloroaniline combines with sodium β -naphthol-3:6-disulphonate to form an azo-dye which yields fast bluish-red lakes. The corresponding compound from 2:4:6-trichloroaniline is quite different in character.

C. H. D.

[Azo-dyes from Nitro-*m*-phenylenediaminesulphonic Acid.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 161277).—Azo-compounds,

yielding fast yellow or orange lakes, are obtained by combining diazo-sulphonic acids of the benzene or naphthalene series with nitro-*m*-phenylenediamine-sulphonic acid. These lakes resist light better than the corresponding compounds from nitro-*m*-diamines (Abstr., 1905, i, 251). This behaviour is exceptional, as an increase in the number of sulphonyl groups usually renders such compounds less suitable for the production of insoluble lakes. C. H. D.

Azo-dyes from Aminoanthraquinonesulphonic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 161151).—Azo-dyes, yielding fast, yellowish-red to bluish-red lakes, are obtained by combining diazotised 1-aminoanthraquinone-2- or -6-sulphonic acid or 1:5-diaminoanthraquinone-2:6-disulphonic acid with α - or β -naphthol-3:6-disulphonic acid. C. H. D.

[1-Hydroxy-4-diazoanthraquinone.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 161954).—In the oxidation of anthraquinone to quinizarin by means of sulphuric acid and sodium nitrate in presence of boric acid and mercury sulphate, an intermediate product, 1-hydroxy-4-diazoanthraquinone sulphate, is formed at 120—150°. On cooling and adding sodium hydroxide, the diazo-compound is precipitated in reddish-brown crystals and may be purified by dissolving in dilute sulphuric acid and precipitating with sodium acetate. Warming with alcohol converts it readily into erythroxyanthraquinone; heating with sulphuric acid at 180° converts it into quinizarin.

C. H. D.

Tri-imides or Azoimides of the Benzidine Series. WILHELM VAUBEL and OTTO SCHEUER (*Zeit. Farb. Text. Ind.*, 1906, 5, 61—62. Compare Vaubel, Abstr., 1900, i, 615; 1903, i, 299).—The action of 1 mol. of nitrous acid on 1 mol. of benzidine hydrochloride in neutral or acid solution at 10—15° leads to the formation of the azoimide or diazoamino-compound, $\begin{matrix} \text{C}_6\text{H}_4\cdot\text{N} \\ | \\ \text{C}_6\text{H}_4\cdot\text{N} \end{matrix} > \text{NH}$ or $\begin{matrix} \text{C}_6\text{H}_4\cdot\text{NH} \\ | \\ \text{C}_6\text{H}_4-\text{N} \end{matrix} \geq \text{N}$, which, on treatment with an excess of hydrochloric acid, is converted into 4-aminodiphenyl-4'-diazonium chloride, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$.

Similar derivatives are obtained from tetrabromobenzidine, tolidine, dibromotolidine, diaminostilbene, diphenetidine, and dianisidine. The azoimides are greyish-brown to brown powders, have no sharp melting point, but decompose and evolve nitrogen at high temperatures, forming at least two decomposition products. G. Y.

Preparation of Sulphineazo-compounds. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 161462).—4-Chloro-1:3-dinitrobenzene condenses with potassium thiocyanate, and the product when reduced yields 2:2'-dinitro-4:4'-diaminodiphenyl disulphide, $\text{S}_2[\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{NH}_2]_2$. The tetrazonium derivative of this combines with phenols, aromatic amines, pyrazolone derivatives, &c., to form *sulphine-azo-dyes*, all of which may be reduced by sodium sulphide to compounds having the constitution $\text{SNa}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{N:N}\cdot\text{X}$. When the component used for the preparation of the azo-compound does not

contain either a carboxyl or a sulphonyl group, and is therefore insoluble in alkalis, it is possible in this way to obtain a soluble product. Air, air and steam, or oxidising agents re-form the insoluble disulphide, metallic salts form insoluble mercaptides, and it is therefore possible to fix the dyes on the fibre. A table of the shades obtained by the use of different components is given. C. H. D.

Polyazo-compounds. KALLE & Co. (D.R.-P. 161720).—Diazonium salts of the general formula $R \cdot N \cdot N \cdot C_6H_4 \cdot N_2 \cdot Cl$, where R is a phenol, amine, or diamine residue prepared from *p*-phenylenediamine, combine in alkaline solution with 1-*p*-aminobenzenediazo-2-amino-5-naphthol-7-sulphonic acid to form dyes of the general formula

$R \cdot N \cdot N \cdot C_6H_4 \cdot N \cdot N \cdot C_{10}H_6(NH_2)(OH)(SO_3H) \cdot N \cdot N \cdot C_6H_4 \cdot NH_2$,
which dye fast blue shades. C. H. D.

Amino-acids, Polypeptides, and Proteids. EMIL FISCHER (*Ber.*, 1906, **39**, 530—610).—A lecture delivered before the German Chemical Society. G. Y.

Yield of Glutamic Acid from Various Proteids. THOMAS B. OSBORNE and RALPH D. GILBERT (*Amer. J. Physiol.*, 1906, **15**, 333—356).—The amount of glutamic acid yielded by various proteids, mainly of vegetable origin, is given. A few quantitative determinations of other products are given also. The object of the research was to find a logical basis for the use of one form of proteid rather than others in nutrition, in health and disease. In animal proteids, the yield of glutamic acid per cent. varies from 7 to 10. In vegetable proteids, with one exception (leucosin of wheat, 5.7 per cent.), the yield is larger (12 to 37 per cent.). W. D. H.

Ovo-vitellin. LOUIS HUGOUNENQ (*Compt. rend.*, 1906, **142**, 173—175).—The various amino-acids obtained by the hydrolysis of vitellin were estimated. The small yield of glycine resembles that from caseinogen, a very similar proteid both as regards its composition and its function as a tissue-forming substance in early life. W. D. H.

Union of Carbon Dioxide with Amphoteric Amino-substances. II. MAX VON SIEGFRIED (*Zeit. physiol. Chem.*, 1905, **46**, 401—414. Compare Abstr., 1905, ii, 332).—The proteids of blood serum, when acted on by carbon dioxide in presence of calcium hydroxide, form calcium salts of proteid carbamic-acids. The preparation and analysis of the pure calcium salts of carbamo-succinic and -glutaric acids and of asparagine-, lysine-, and arginine-carboxylic acids is described. It is shown that alanine and glycine are converted by carbon dioxide in aqueous solution into the corresponding carbamic acids. E. F. A.

Crude Gluten. F. A. NORTON (*J. Amer. Chem. Soc.*, 1906, **28**, 8—25).—Crude gluten contains about 75 per cent. of pure gluten (gliadin and glutenin) and small amounts of non-gluten proteid,

mineral matter, fat, starch, and fibre. Its relation to the total proteid ($N \times 5.7$) varies in different flours, the amount being greater than that of total proteid in low-grade flours, nearly the same in patent flours, and less in whole wheat meal.

The determination of crude gluten is of little use in the valuation of flours. The best simple method for estimating the gluten content and ascertaining the character of the gluten seems to be the determination of total and gliadin nitrogen with expression of the ratio of gliadin to total proteid ($N \times 5.7$). N. H. J. M.

Separation of the Phosphorus from Caseinogen by Enzymes and Alkali. R. H. ADERS PLIMMER and WILLIAM M. BAYLISS (*J. Physiol.*, 1906, 33, 439—461).—Trypsin converts the whole of the phosphorus of caseinogen into a soluble form in twenty-four hours, except for a small insoluble residue derived partly from the trypsin and partly from the caseinogen, and consisting probably of decomposition products of nucleo-proteid. The curve for the rate of separation of the phosphorus runs parallel to that for the increase in electrical conductivity for the first eight hours; then it is less rapid. The soluble phosphoric acid consists of inorganic phosphoric acid (35 per cent.) and an organic compound (65 per cent.). Pepsin produces a similar change, but exceedingly slowly. Papain, acting best in a neutral or faintly acid medium, is intermediate in the rate at which it acts. Ovo-vitellin containing lecithin is digested slowly as compared with caseinogen. One per cent. sodium hydroxide resembles trypsin in its rate of action, and the product is wholly inorganic phosphoric acid. The organic compound of phosphorus obtained by tryptic action is not completely converted into inorganic phosphoric acid by 1 per cent. sodium hydroxide. The total quantity of inorganic phosphoric acid obtained by the successive use of the two reagents is 50 per cent. of the total phosphorus of the caseinogen. W. D. H.

Jecorin. MAX SIEGFRIED and H. MARK (*Zeit. physiol. Chem.*, 1905, 46, 492—495).—Jecorin is regarded as being a definite substance, and not a mixture, as Meinertz states (this vol., i, 124). W. D. H.

Composition of "Dichromated" Gelatin which has Spontaneously become Insoluble in the Dark. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1906, [iii], 35, 14—16. Compare Abstr., 1905, i, 847, 848).—Films of gelatin spread on glass were treated with a 3 per cent. solution of potassium dichromate while exposed in the dark, at ordinary temperatures or at 120° , until they had become insoluble in water at 80° . They were then washed and analysed.

The films prepared at the ordinary temperature were exposed for one, two, or four and half months; they contained 0.67, 0.93, and 1.15 per cent. of chromium sesquioxide, and 1.19, 0.46, and 0.22 per cent. of ash respectively, but did not contain any chromium trioxide.

The films prepared at 120° were exposed in the dark for one and six days, and contained 0.54 and 2.72 per cent. of chromic acid, 8.68 and

20.59 per cent. of chromium sesquioxide, and 0.06 and 0.1 per cent. of ash respectively.

The results show that "insoluble gelatin," prepared in the dark at the ordinary temperature, contains smaller quantities of chromium sesquioxide than that produced by exposure to light (*loc. cit.*), and is also less resistant to the action of boiling water. That prepared at 120° in the dark is quite insoluble in boiling water, but is broken up by it into small fragments, and, like "insoluble gelatin" prepared by exposure to light, appears to contain some uncombined chromium sesquioxide, produced by direct reduction of the dichromate by the gelatin.

Similar experiments made with films of gelatin on paper gave unsatisfactory results owing to the difficulty of entirely removing the paper before analysis.

T. A. H.

Formation of a Dipeptide by Hydrolysis of Silk Fibroin.

EMIL FISCHER and EMIL ABDERHALDEN (*Ber.*, 1906, 39, 752—760. Compare Abstr., 1903, i, 694).—The successive hydrolysis of silk fibroin by sulphuric acid and pancreatin yields tyrosine and a syrup containing amino-acids, di- and poly-peptides. The dipeptides were isolated in the following way. The syrup, dissolved in alcohol, was esterified by hydrogen chloride, and the solution, after removal of the mineral acid by sodium ethoxide, was evaporated below 65° under 10 mm. pressure, the distillate containing a small quantity of ethyl aminoacetate. The residual greenish-brown syrup was dissolved in alcohol and treated in the cold with dry ammonia, whereby *diketomethylpiperazine*, $\text{NH} \begin{matrix} \text{CH}_2 - \text{CO} \\ \text{CO} \cdot \text{CHMe} \end{matrix} \text{NH}$, and a small quantity of glycine-tyrosine anhydride were precipitated, the former being finally obtained pure in the form of small needles. It resembles *i*-glycine-alanine anhydride (Abstr., 1903, i, 608), except that it has $[\alpha]_D - 3.9^\circ$ at 20°. It is hydrolysed by hydrochloric acid, forming glycine and *d*-alanine, and by treatment with sodium hydroxide at the ordinary temperature forms a dipeptide which is probably a mixture of glycyl-*d*-alanine and *d*-alanylglycine. It does not depress the melting point of synthetical glycine-*d*-alanine anhydride, with which it is identical, but has a smaller rotatory power, due to the partial racemisation which occurs during the hydrolysis of silk fibroin by sulphuric acid. A better yield of the compound is obtained when the complex products of the hydrolysis are removed by means of phosphotungstic acid before esterification. The hydrolysis of silk fibroin with hydrochloric acid of sp. gr. 1.19 gives a 12 per cent. yield of diketomethylpiperazine, and shows that the formation of this compound is not due to the action of the pancreatin. Experiments were successfully performed which indicate that the production of the compound is not due to a secondary reaction between the primarily formed glycine and *d*-alanine.

C. S.

Crystalline Urinary Albumose. II. ALIDE GRUTTERINK and

C. J. WEEVERS DE GRAAFF (*Zeit. physiol. Chem.*, 1905, 46, 472—481).—The Bence-Jones proteid, which sometimes is obtainable in crystalline

form from urine, is regarded as more akin to a native proteid than to an albumose. It yields, on digestion, products analogous to those obtainable from albumin.

W. D. H.

Peptone. II. LYMAN B. STOOKEY (*Proc. Amer. Physiol. Soc.*, 1905, xii—xiii; *Amer. J. Physiol.*, 15).—A preliminary statement in regard to a fraction obtained by benzoyl chloride, but the findings are not regarded as conclusive.

W. D. H.

Proteid Peptone. LYMAN B. STOOKEY (*Beitr. chem. Physiol. Path.*, 1906, 7, 590—595).—From the products of peptic digestion of blood-albumin, benzoyl, benzenesulphonyl, and naphthalenesulphonyl products of peptone were separated. The composition and reactions of these are compared, but, owing to the necessity of abandoning the work prematurely, the products were not defined with necessary exactitude.

W. D. H.

Comparison of Ferments and Lysins. E. W. AINLEY WALKER (*Proc. Physiol. Soc.*, 1905, xxi—xxiv; *J. Physiol.*, 33).—Examples are given which support the provisional view that ferments are double substances, consisting of a specific amboceptor and a non-specific kinase or complement. Bacteriolysis and similar phenomena are thus to be regarded as special cases of a general physiological reaction.

W. D. H.

Influence of Reaction on the Activity of Amylase. LÉON MAQUENNE and EUGÈNE ROUX (*Compt. rend.*, 1906, 142, 124—129).—The optimum reaction at which amylase acts on various kinds of starch is that of exact neutrality. Starch solutions and solutions of amylase from malt are usually alkaline, so that enough acid (sulphuric or hydrochloric) must be added to neutralise both, helianthin being used as indicator. The sugar formed is wholly maltose.

W. D. H.

Influence of the Reaction of the Medium on the Activity of Diastases. AUGUSTE FERNBACH (*Compt. rend.*, 1906, 142, 285—286).—In experiments on the action of very small amounts of amylase on an excess of starch, it was found that the action was quickest under conditions of neutrality to helianthin. The results of Maquenne and Roux, indicating that an alkaline reaction is most favourable [compare, however, preceding abstract], is attributed to a large excess of malt extract and a small amount of starch having been employed.

N. H. J. M.

Action of Invertin in a Heterogeneous Medium. VICTOR HENRI (*Compt. rend.*, 1906, 142, 97—100).—The rate of the inversion of sucrose by a mixture of gelatin and invertin, separated from the sucrose solution by a thin layer of pure gelatin, is nearly proportional to the strength of the sucrose solution. When, however, the invertin is present in the solution itself, the inversion is about the same in the two solutions of different strengths. Variations in temperature have much less effect on the inversion of sucrose when the invertin is mixed with gelatin than when it is present in the solution.

The concentration of substances transformed by the ferment will influence the rate of digestion when the ferments are endocellular, but not when they are distributed in the liquids of the organism.

N. H. J. M.

Enzyme Action. II. H. P. BARENDRECHT (*Zeit. physikal. Chem.*, 1906, 54, 367—375).—The conversion of lactose into galactose and dextrose by the action of lactase (obtained from *Saccharomyces kephir*) has been studied on the lines of the author's earlier work (Abstr., 1904, ii, 551, 719). The conversion is retarded twice as much by galactose as by dextrose, and about as much by a molecule of lævulose as by a molecule of galactose and a molecule of dextrose together.

It is found that the inversion of sucrose by invertase, obtained from kephir yeast, is less retarded by dextrose, lævulose, and galactose than inversion by invertase obtained from ordinary yeast.

In confirmation of Brown's observation (*Trans.*, 1902, 81, 382), the author finds that lactose exerts practically no retarding influence on the inversion of sucrose by ordinary invertase, a result which is interpreted in terms of the theory previously brought forward (*loc. cit.*).

Emphasis is laid on the fact, demonstrated by the author's work, that the action of enzymes on bioses is retarded much less by the hexoses produced in the reaction than by other hexoses. J. C. P.

Action of Lipase. ARTHUR S. LOEVENHART (*Proc. Amer. Physiol. Soc.*, 1905, xxvii—xxviii; *Amer. J. Physiol.*, 15).—The substance in liver extracts which Magnus termed the co-ferment of lipase is bile salts. Observations also show that the enzyme lipase is probably different from that which causes hydrolysis of esters. But the existence of such an enzyme, esterase, is to be considered in a later paper. W. D. H.

Action of Papain. C. DELEZENNE, H. MOUTON, and E. POZERSKI (*Compt. rend.*, 1906, 142, 177—179).—Papain acts best in a slightly acid medium, and forms from albumin the usual proteolytic products. The action follows the law of square roots formulated by Schütz. In some prolonged experiments, an increase of coagulable proteid occurs in the later stages of digestion, a phenomenon regarded as indicating a reversible action, or due to the formation of plasteins. W. D. H.

Pancreas Steapsin and the Velocity of Fat Hydrolysis produced by Enzymes. ARISTIDES KANITZ (*Zeit. physiol. Chem.*, 1905, 46, 482—491).—A steapsin extract, prepared by digesting an ox or pig's pancreas for a considerable time with glycerol, brings about the rapid hydrolysis of olive oil. This change follows the law $x/\sqrt{t} = \text{a constant}$; x being the amount hydrolysed in time t .

The cases studied by Connstein, Hoyer and Wartenberg (Abstr., 1903, i, 218) and by Zellner (Abstr., 1905, ii, 550) are shown to obey the same law. E. F. A.

Organic Chemistry.

The Series C_nH_{2n-2} in Louisiana Petroleum. CHARLES E. COATES (*J. Amer. Chem. Soc.*, 1906, 28, 384—388. Compare Coates and Best, *Abstr.*, 1905, ii, 833).—The crude oil from Jennings, which is the lightest Louisiana petroleum, contains a small proportion of saturated hydrocarbons of comparatively low molecular weight, which have an odour resembling that of turpentine but are optically inactive. The following hydrocarbons were separated by repeated fractional distillation. The *hydrocarbon*, $C_{10}H_{18}$, boils at 168—170° under 760 mm. pressure, has a sp. gr. 0·8146 at 22°/4°, and n_D 1·4460 at 25°. The *hydrocarbon*, $C_{11}H_{20}$, boils at 198—200° under 760 mm. pressure, has a sp. gr. 0·8378 at 26°/4°, and n_D 1·4582 at 25°. The *hydrocarbon*, $C_{12}H_{22}$, boils at 215—217° under 760 mm. pressure, has a sp. gr. 0·8511 at 28°/4°, and n_D 1·4640 at 25°. The *hydrocarbon*, $C_{15}H_{24}$, boils at 235—238° under 760 mm. pressure, has a sp. gr. 0·8629 at 22°/4°, and n_D 1·4692 at 25°.

Small fractions were obtained which probably consisted of the hydrocarbons C_8H_{14} and C_9H_{18} . The former boiled at 120·5°, had a sp. gr. 0·7747 at 24°/4°, and n_D 1·4260 at 25°. The latter boiled at 145·7°, had a sp. gr. 0·7992 at 24°/4°, and n_D 1·4370 at 25°. E. G.

The Alcoholic Function. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1905, 537—554. Compare this vol., i, 133).—It is pointed out that, by reason of their great reactivity with the halogen acids, acid anhydrides, and acid chlorides, the tertiary alcohols should be regarded as the organic analogues of potassium hydroxide, whilst the primary and secondary alcohols in their behaviour with these reagents more closely resemble water.

Thus the secondary alcohol, methyl*tert*.butylcarbinol, is converted completely by acetyl chloride into the acetate, which boils at 143° under 757 mm. pressure. Its isomeride, dimethylisopropylcarbinol, on the contrary, with the same reagent yields acetic acid and dimethylisopropyl chloride. When a mixture of equal quantities of trimethylcarbinol and isobutyl alcohol is saturated with hydrogen chloride at atmospheric temperature, the former alcohol is converted into the corresponding chloride, but the latter is not acted on. The results of a number of similar experiments are quoted, illustrating the author's contention. T. A. H.

Formation of Alcoholates by Certain Salts in Solution in Methyl and Ethyl Alcohols. HARRY C. JONES and LEROY McMASTER (*Amer. Chem. J.*, 1906, 35, 316—326. Compare Jones and Getman, *Abstr.*, 1904, ii, 386, 711).—The molecular elevation of the boiling point of methyl alcohol produced by lithium chloride, bromide, and nitrate has been determined. The results are tabulated and lead to the conclusion that alcoholates are formed in the solutions, and that

as the concentration of the solution becomes greater a larger proportion of alcohol is held in combination and the molecular rise in boiling point therefore increases.

Determinations have also been made of the molecular elevation of the boiling point of ethyl alcohol brought about by lithium chloride, bromide, and nitrate, and calcium nitrate. The results obtained confirm those of Jones and Getman (Abstr., 1904, ii, 711).

E. G.

Rise of Temperature when Chloroform and Ethyl Ether are Mixed. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1906, 244, 24—25).—When 59.5 grams of chloroform and 37.0 grams of ethyl ether, both at 15.2°, are mixed, the temperature of the mixture rises to 30.2°.

C. F. B.

Thiocarbonates. B. HOLMBERG (*J. pr. Chem.*, 1906, [ii], 73, 239—248. Compare Abstr., 1905, i, 323).—The action of carbon dioxide on potassium hydrogen sulphide in alcoholic solution leads to the formation of hydrogen sulphide and a mixture of potassium hydrogen carbonate and potassium ethyl carbonate, which, contrary to Chancel's statement (*Jahresb.*, 1851, 513), are formed also by the interaction of carbon dioxide and potassium ethyl mercaptide in alcoholic solution.

The action of carbonyl sulphide on potassium hydrogen sulphide in alcoholic solution leads to the formation of hydrogen sulphide and potassium ethyl thiocarbonate, which is formed also by the interaction of carbonyl sulphide and potassium ethyl mercaptide in alcoholic solution. On the other hand, the action of carbonyl sulphide on potassium ethyl mercaptide in aqueous solution leads to the liberation of the mercaptan and formation of potassium hydrogen carbonate.

The author confirms his statement, in opposition to Büllmann (*Diss.*, Copenhagen, 1904, 1905), that the action of carbon disulphide on potassium hydrogen sulphide in alcoholic solution leads to the formation of potassium trithiocarbonate, potassium xanthate, and hydrogen sulphide.

Potassium ethyl trithiocarbonate, formed by the action of carbon disulphide on potassium ethyl mercaptide in alcoholic solution, crystallises in intensely yellow, stout needles or prisms (compare Chancel, *loc. cit.*), and, on addition of hydrochloric acid, yields ethyl hydrogen trithiocarbonate as a heavy, red oil of unpleasant odour.

When boiled in neutral or alkaline solution, trithiocarbodiglycollic acid yields thioglycollic acid and ammonium thiocyanate, and not thiocarbamide, as stated previously (*loc. cit.*).

G. Y.

Fatty Acids of Brain Lecithin. H. COUSIN (*J. Pharm. Chim.*, 1906, [vi], 23, 225—230).—The lecithin was isolated from cow brains by a modification of Thudichum's process, and was saponified by heating with a solution of sodium hydroxide in alcohol. The method of separating and identifying the fatty acids used was the same as that previously employed (Abstr., 1903, i, 675). Stearic, palmitic, and oleic acids were identified. In addition, an oily acid was obtained, having an iodine value 129; this is being studied further

and may prove to be linoleic acid. Choline and glycerophosphoric acid were also found among the hydrolytic products. T. A. H.

Composition of Lecithins. M. WINTGEN and O. KELLER (*Arch. Pharm.*, 1905, 244, 3—11).—Samples of lecithins of different origin gave the following results on analysis :

	N per cent.	P per cent.	Ratio N : P.
<i>Distearyl-lecithin</i> (calculated).....	1·73	3·84	1 : 2·22
Coml. lecithin from yolk of egg.....	2·25	3·49	1 : 1·55
" " purified.....	2·37	3·78	1 : 1·59
Egg-lecithin, prepared by authors :			
from ethereal extract	2·50	3·09	1 : 1·48
from alcoholic extract	2·51	3·57	1 : 1·52
Lecithin, prepared by authors :			
from brown Soja beans.....	1·90	2·96	1 : 1·56
from black Soja beans	1·84	2·51	1 : 1·27

C. F. B.

Electrolysis of the Alkali Salts of Organic Acids. IV. JULIUS PETERSEN (*Zeit. Elektrochem.*, 1906, 12, 141—145. Compare Abstr., 1898, i, 352, and 1900, ii, 522).—When a solution of the potassium salt of α -methylbutyric acid is electrolysed, the products are trimethylcarbinyl α -methylbutyrate, $\gamma\delta$ -dimethylhexane, Δ^{β} -butylene ($\text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{CH}_3$), carbon dioxide, hydrogen, and a little oxygen. The quantity of butylene increases as the current density increases, and also as the solution becomes more dilute.

When electrolysed in a warm dilute alcoholic solution, potassium laurate yields, mainly, the hydrocarbon docosane ($\text{C}_{22}\text{H}_{46}$) and small quantities of ethyl laurate. Myristic, palmitic, and stearic acids behave in the same way, yielding a hexacosane, $\text{C}_{26}\text{H}_{54}$, melting at $56\cdot6^\circ$ (89·1 per cent. of the theoretical quantity), triacontane, $\text{C}_{30}\text{H}_{62}$, melting at $66\cdot1^\circ$ (88·1 per cent.), and tetratriacontane, $\text{C}_{34}\text{H}_{70}$, melting at $72\cdot9^\circ$ (73·6 per cent.) respectively. T. E.

Reagent in the Chemistry of Fats. ERNEST TWITCHELL (*J. Amer. Chem. Soc.*, 1906, 28, 196—200).—Sulphophenyl- and sulphonaphthylstearic acids (Abstr., 1900, i, 296) are found to act as catalytic agents in the hydrolysis of fats. If 1 per cent. of sulphonaphthylstearic acid is boiled with a mixture of fat and water, an almost complete separation of the glycerol is effected in eight to ten hours. A comparison of the hydrolysing power of *N*/75 sulphonaphthylstearic acid and *N*/75 hydrochloric acid on triacetin has shown that these acids are equally effective, but that if an insoluble glyceride is substituted for the triacetin, the hydrochloric acid has practically no effect, whilst the sulphonaphthylstearic acid acts at approximately the same rate as it does on the soluble esters. The property of these sulphostearic acids of dissolving in both fatty acid and water and rendering them mutually soluble has been applied to the separation of solid and liquid fatty acids. E. G.

Ethyl Tetrolate. FRANZ FEIST (*Annalen*, 1906, **345**, 100—116).—Attempts have been made to ascertain whether the acetylene linking of ethyl tetrolate, $\text{CH}_3\cdot\text{C}\equiv\text{C}\cdot\text{CO}_2\text{Et}$, will bring about condensations of the methyl group with ketone groups in the presence of sodium ethoxide. Although the ester is very reactive, no simple condensation products could be obtained.

Tetrolic acid was prepared by a modification of Desprez's method. *Ethoxycrotonic acid*, $\text{OEt}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, was obtained as a by-product; it formed leaflets melting at 141° , and when boiled with water was decomposed with the elimination of carbon dioxide. Ethyl tetrolate could be prepared by the usual method; the use of phosphorus pentachloride to form the acid chloride, which might then be used for obtaining the ester, leads to the production of chlorocrotonic acids.

Benzaldehyde and ethyl tetrolate react readily in the presence of sodium, giving the substance $(\text{C}_9\text{H}_8\text{O}_2)_x$, which melts and decomposes at 125° ; it is not ethyl benzylidenetetrolate. Acetophenone and ethyl tetrolate yield an oil which is possibly the compound $\text{COPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}\cdot\text{Me}$. Ethyl acetoacetate is the only product of the action of ethyl tetrolate and ethyl oxalate which could be isolated.

Ethyl tetrolate does not react with sodamide, but in the presence of this reagent yields sodium salts with acetone, acetophenone, and ethyl oxalate. The condensation products could not be isolated; an attempt to couple the product obtained when ethyl oxalate was used with *p*-nitrophenylhydrazine gave a complex substance, $\text{C}_{17}\text{H}_{19}\text{O}_7\text{N}_3$, which is a yellow powder melting and decomposing at 74° and soluble in alkali hydroxides with a violet coloration.

With a concentrated aqueous or alcoholic solution of ammonia, ethyl tetrolate yields ethyl β -aminocrotonate, but with dilute solutions of ammonia, tetrolamide, $\text{CMe}\cdot\text{C}\cdot\text{CO}\cdot\text{NH}_2$, is formed. It was obtained as white crystals from water, melting at 147 — 148° . With *p*-nitrophenylhydrazine in the presence of mercuric chloride, 1-*p*-nitrophenyl-3-methylpyrazolone (m. p. 214°) is formed, and with benzenediazonium chloride in the presence of sodium acetate, *phenylazoacetoacetamide*, $\text{NPh}\cdot\text{NC}\cdot\text{HAc}\cdot\text{CO}\cdot\text{NH}_2$, crystallising in needles melting at 145° . Ethyl tetrolate and piperidine yield *ethyl piperidinocrotonate*, which is a syrup giving a violet coloration with ferric chloride in alcoholic solution, and decomposes, yielding the piperidide of tetrolic acid, which melts at 238° . With aniline, ethyl tetrolate seems to form an anilide, which then combines with water producing acetoacetanilide, which reacts with the excess of aniline, yielding acetone and diphenylcarbamide.

Ethyl tetrolate and phenylhydrazine react in solution in high boiling petroleum, yielding 1-*phenyl-3-methyl-5-pyrazolone*, which forms crystals melting at 127° , and is converted by ferric chloride into pyrazole-blue; at the same time, bisphenylmethylpyrazolone is formed by the action of the pyrazolone with excess of phenylhydrazine: it is not molten at 320° ; this reaction would indicate that the ethyl tetrolate and phenylhydrazine first form the phenylhydrazone of ethyl acetoacetate. Ethyl tetrolate and ethyl diazoacetate react at 140° , yielding the condensed additive product, *ethyl 4-methylpyrazole-3:5-*

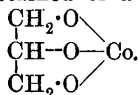
dicarboxylate, $\text{NH} \begin{array}{c} \text{N} \text{-----} \text{C} \cdot \text{CO}_2\text{Et} \\ \text{C}(\text{CO}_2\text{Et}) \cdot \text{CMe} \end{array}$, which melts at 104° , or, when anhydrous, at $106\text{--}107^\circ$, and can be hydrolysed to the corresponding acid (melting and decomposing at 305°). K. J. P. O.

***l*-Lactic Acid.** EMILE JUNGFLEISCH and MARCEL GODCHOT (*Compt. rend.*, 1906, **142**, 515—518).—*l*-Lactic acid was prepared from quinine *l*-lactate (Abstr., 1904, i, 645) through the zinc salt by the process already described (Abstr., 1905, i, 318). Zinc *l*-lactate closely resembles zinc *d*-lactate in appearance, has similar solubilities, and approximately the same specific rotations, in an opposite sense, for the same concentrations of solution. *l*-Lactic acid crystallises in flattened prisms similar to those formed by the dextro-acid, is very hygroscopic, melts at $26\text{--}27^\circ$, and has a specific rotation which diminishes with increasing dilution of the solution. The specific rotations observed are practically equal to those of the *dextro* acid, but are of opposite sign. The *laevo* acid, like the dextro and racemic isomerides, changes spontaneously in concentrated solutions, forming *l*-lactyl-lactic acid (Abstr., 1905, i, 259), which is dextrorotatory. This explains the change in the sign of the rotation of *l*-lactic acid when an aqueous solution is evaporated (compare Abstr., 1905, i, 630). *l*-Lactyl-lactic acid is reconverted into *l*-lactic acid when its aqueous solution is heated in a closed tube at 100° for several hours. It is pointed out that Mackenzie (*Trans.*, 1905, **87**, 1373) is in error in assuming that Jungfleisch has withdrawn his statement (Abstr., 1904, i, 796) that *l*-lactic acid is more readily racemised than *d*-lactic acid (compare Abstr., 1905, i, 319). T. A. H.

The Lactide of *l*-Lactic Acid. ÉMILE JUNGFLEISCH and MARCEL GODCHOT (*Compt. rend.*, 1906, **142**, 637—639. Compare Abstr., 1905, i, 259, 318, 630).—When anhydrous *l*-lactic acid is distilled at $150\text{--}155^\circ$, a mixture of *l*- and *i*-lactides is obtained, from which the two constituents are readily separated by fractional crystallisation from ether. *l*-Lactide forms orthorhombic crystals enantiomorphously related to the *d*-lactide crystals (Wyruboff), whilst in respect of melting point, boiling point, and solubility the two isomerides are identical. *l*-Lactide is dextrorotatory, and the rotation diminishes as the dilution is increased; solutions containing 0.8158 gram, 0.4079 gram, or 0.2039 gram per 100 c.c. of benzene have $[\alpha]_D +281.6^\circ$, $+268^\circ$, or $+231^\circ$ respectively at 16° . *l*-Lactide undergoes progressive hydrolysis in contact with cold water, forming *l*-lactyl-lactic acid and *l*-lactic acid: thus a solution of 0.1422 gram of *l*-lactide in 30 c.c. of water immediately after solution and after 2, 6, 12, 18, 42, 66, and 80 hours has $[\alpha]_D +204^\circ$, $+140^\circ$, $+114^\circ$, $+91^\circ$, $+42^\circ$, $+35^\circ$, $+28^\circ$, and $+14^\circ$ respectively at 12° . *i*-Lactide is readily obtained by mixing equivalent quantities of *l*- and *d*-lactide in ethereal solution. M. A. W.

Tervalent Cobalt and Nickel. STANLEY R. BENEDICT (*J. Amer. Chem. Soc.*, 1906, **28**, 171—177).—A solution of cobaltioxalic acid, $\text{H}_6\text{Co}_2(\text{C}_2\text{O}_4)_3$, can be obtained by boiling a solution of a cobalt salt with

sodium peroxide, collecting and washing the black cobaltic hydroxide, and dissolving it by pouring a cold saturated solution of oxalic acid on it whilst still on the filter. When this solution is left for a few hours its colour changes from green to pink, and cobaltous oxalate is precipitated. This reduction is only slightly accelerated by sulphurous acid or hydrogen sulphide. If the solution is made alkaline with sodium carbonate, it is not appreciably reduced by boiling, and does not appear to be affected by ferrous salts or stannous chloride. The calcium salt crystallises in dark green needles with $6\text{H}_2\text{O}$, and is very stable towards reducing agents. A method is described for the preparation of the potassium salt which is more rapid than either of those described by Kehrmann (Abstr., 1887, 220) or Marshall (Trans., 1891, 59, 760). When a solution of a cobalt salt is treated successively with glycerol, sodium hydroxide, and bromine water, and the mixture is boiled, a black solution is obtained of a compound which is probably



A solution of nickelic acetate can be obtained by dissolving freshly precipitated nickelic hydroxide in well-cooled 90 per cent. acetic acid. This solution gradually undergoes reduction in the cold, instantaneously on warming, and is immediately reduced by all reducing agents. Similar solutions can be obtained by the action of citric and tartaric acids on nickelic hydroxide. When freshly precipitated nickelic hydroxide is treated with a nearly saturated solution of potassium hydrogen sulphate, a solution is obtained which is a powerful oxidising agent and contains either a simple or complex nickelic sulphate. When cobaltic hydroxide is treated in this way, a cobaltic sulphate is not produced. E. G.

Ethyl Carbacetoacetate and Ethyl isodehydroacetate. FRANZ FEIST [with OTTO BEYER] (*Annalen*, 1906, 345, 60—99).—It is still uncertain whether the ethyl carbacetoacetate prepared by Duisberg by the action of hydrogen chloride on ethyl acetoacetate is identical with the ethyl isodehydroacetate prepared by Hantzsch by the action of concentrated sulphuric acid on ethyl acetoacetate. Genvresse believed that he had shown that the two esters were distinct, whilst Hantzsch and Polonowska maintained that they were identical. It is, however, found that they are identical, the so-called ethyl carbacetoacetate being only an impure ethyl isodehydroacetate.

Ethyl isodehydroacetate (ethyl carbacetoacetate) was prepared by Duisberg and Genvresse's methods, but did not give correct analytical numbers until it had been fractionated several times; it melts at 15° and distils without decomposition at 177° under 16 mm. pressure, and when pure gives no coloration with ferric chloride (compare Genvresse). Its molecular weight was determined by Beckmann's method in ether.

The monobromo-derivative of ethyl carbacetoacetate described by Genvresse was found not to exist, the ethyl bromoisodehydroacetate, which melts at 87° , being alone obtained; it crystallises in the mono-

clinic system [$\alpha : \beta : \gamma = 0.5891 : 1 : 0.32796$; $\beta = 95^\circ 22'$]. When hydrolysed with aqueous potash, methyl trimethenyldicarboxylic acid (m. p. 200°), which was obtained by Genvresse, was alone produced.

Ethyl chloroisodehydroacetate was also prepared by Genvresse's method; although identical in properties (m. p. $57-58^\circ$) with Genvresse's ethyl chlorocarbacetoacetate, the analyses showed that it was a derivative of the isodehydroacetate.

The products of hydrolysis of the isodehydroacetate by barium or sodium hydroxide were identical with those obtained by Genvresse by the use of the former base, a mixture of *cis*- and *trans*- β -methylglutaconic acids being formed. Hantzsch and Anschütz, who had used only a very concentrated solution of a base instead of the 2*N* NaOH solution used here, only observed the formation of the *trans*-acid.

The hydrolysis is effected by boiling the ester with 3—4 molecules of sodium hydroxide (2*N*) for eight to ten minutes; the yield of the *cis*-acid is increased by use of the smaller amount of base. The two acids are separated by successive fractional extraction of the mixture with ether, chloroform, and water. *trans*- β -Methylglutaconic acid can also be prepared by the addition of ethyl sodiomalonate to ethyl tetrolate; the ester thus obtained is purified by fractionation and boils at $260-270^\circ$. It is converted into the β -methylglutaconic acid by hydrolysis with sodium hydroxide, and melts at $115-116^\circ$, the melting point of Genvresse's compound. The calcium salt prepared from both acids crystallises with $4\text{H}_2\text{O}$ and the barium salt with $2-3\frac{1}{2}\text{H}_2\text{O}$, but not with $6\text{H}_2\text{O}$, as stated by Genvresse; the silver salt, $2\text{C}_6\text{H}_6\text{O}_4\text{Ag}_2 \cdot \text{AgOH} \cdot \text{H}_2\text{O}$, was also prepared. This acid combines with bromine but slowly, the product yielding when hydrolysed methyltrimethenyldicarboxylic acid. With hydrogen bromide, bromo- β -methylglutaric acid is obtained, melting at 129° . Ethyl $\alpha\beta$ -dibromo- β -methylglutarate, $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{CBrMe} \cdot \text{CHBr} \cdot \text{CO}_2\text{Et}$, is obtained by the combination of bromine with ethyl β -methylglutaconate and is an oil which cannot be distilled. When hydrolysed with alkali hydroxides, it behaves in two different ways, according to the quantity of base used. With excess of potassium hydroxide, *trans*- β -methylglutaconic acid together with a small quantity of the *cis*-form is produced. With the calculated quantity of base, ethyl α -hydroxy- β -methylglutaconate, $\text{CO}_2\text{Et} \cdot \text{CH} \cdot \text{CMe} \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{Et}$, which is an oil boiling at $265-270^\circ$, is formed; in the latter case, hydrogen bromide is eliminated and the second bromine atom replaced by a hydroxyl group. It is noted that in the action of potassium hydroxide on the dibrominated ester, methyltrimethenyldicarboxylic acid is not formed.

cis- β -Methylglutaconic acid, obtained both by the action of an alkali hydroxide on ethyl isodehydroacetate and on the so-called ethyl carbacetoacetate, is shown to be identical both with Hantzsch's "homomesaconic" acid and with Genvresse's acid; the correct melting point is 146.5° , whilst Hantzsch records 147° and Genvresse 141° . The latter fact, together with some other reactions, led Genvresse to regard his acid as distinct from Hantzsch's. The calcium salt, $\text{C}_6\text{H}_6\text{O}_4\text{Ca} \cdot 4\text{H}_2\text{O}$, is crystalline, the barium salt crystallises in leaflets with $5\text{H}_2\text{O}$, and the copper salt (with $2\text{H}_2\text{O}$) is a pale bluish-green precipitate.

The acid obtained by Anschütz, Bendix, and Kerp by the action of excess of highly concentrated alkali hydroxide on ethyl isodehydroacetate has been investigated; their observations have been confirmed; two acids are formed: one in very small quantity, melting at 149° , and a second, which is always present in a much greater proportion, melts at 234° (Anschütz, 228°). Alteration of the concentration of the alkali hydroxide within certain limits only changes to a small extent the proportion of the two acids. Analyses and molecular weight determinations show the formula of the acid melting at 234° to be $C_{15}H_{18}O_6Me_3$. K. J. P. O.

β -Methylglutaconic Acid and $\alpha\beta$ -Dimethylglutaconic Acid. FRANZ FEIST and OTTO BEYER (*Annalen*, 1906, 345, 117—126).—The two β -methylglutaconic acids, which have been obtained both by Genvresse and the authors from ethyl isodehydroacetate (preceding abstract), show that Thorpe (*Trans.*, 1905, 87, 1669) was in error in concluding that only the *trans*- β -methylglutaconic acid (m. p. 149°) is capable of existence. His view, therefore, as to the influence of a methyl group on the stereoisomerism shown by these acids is no longer supported by the experimental evidence.

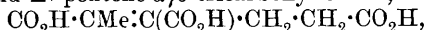
It is found, however, that the presence of this methyl group greatly reduces the reactivity of the neighbouring CH group.

In order to demonstrate with greater certainty the constitution of β -methylglutaconic acid, it was reduced by hydriodic acid and red phosphorus to β -methylglutaric acid (m. p. 85 — 86°). Ethyl β -methylglutaconate was converted into ethyl $\alpha\beta$ -dimethylglutaconate by heating with methyl iodide and sodium in the presence of a small quantity of alcohol at 120° under pressure. The $\alpha\beta$ -dimethyldiglutaaconic acid obtained by hydrolysis of this ester had all the properties ascribed to it by Thorpe (*loc. cit.*) and melted at 145° .

Ethyl β -methylglutaconate readily condenses with benzaldehyde, yielding when hydrolysed α -benzylidene- β -methylglutaconic acid, melting and decomposing at 169° . With diazonium salts, nitrous acid, and nitrosodimethylaniline, the ester reacts but slowly. K. J. P. O.

Antimony Tartrate. J. BOUGAULT (*Compt. rend.*, 1906, 142, 585—586).—The product $SbC_4H_5O_7$, prepared by Guntz's process (*Abstr.*, 1887, 657), is a mixture of antimony tartrate with an ethyl ether of antimony tartrate. If the alcohol used in this process is replaced by acetone, the *antimony tartrate* obtained has the composition $SbC_4H_3O_6$, that is, it contains a mol. of water less than Guntz's product, due probably to an internal esterification between a carboxyl and a hydroxyl group of the acid. It crystallises in small lamellæ, dissolves in 125 parts of water, and is dissociated when diffused in a quantity of water insufficient to dissolve it. The salt gives all the reactions of "tartar emetic," which may be prepared from it by solution in the necessary quantity of an aqueous solution of potassium hydrogen carbonate. Its solubility in aqueous solutions of potassium acetate and potassium hydrogen carbonate serve to distinguish it from antimony ethyl tartrate. T. A. H.

Constitution of Hæmatic Acid. WILLIAM KÜSTER [with H. GALLER, K HAAS and OTTO MEZGER] (*Annalen*, 1906, 345, 1—59. Compare Abstr., 1901, i, 58, 298).—The constitution of the hæmatic acids, $C_8H_8O_5$ and $C_8H_9O_4N$, previously suggested (Abstr., 1902, i, 845), which denotes them as the anhydride and imide respectively of the acid $\Delta\gamma$ -pentene- $\alpha\gamma\delta$ -tricarboxylic acid,



has been confirmed by a series of detailed experiments.

Methylethylmaleic anhydride, $\begin{matrix} CMe \cdot CO \\ | \\ CEt - CO \end{matrix} > O$, could not be prepared by

the condensation of methylsuccinic acid and pyruvic acid in the presence of acetic anhydride, but was obtained from methyl ethylacetacetate; the latter was condensed with hydrogen cyanide in ethereal solution, and the product of the reaction immediately hydrolysed with hydrochloric acid; the anhydride, which was purified by means of the *barium* salt, $C_7H_8O_4Ba \cdot H_2O$, is an oil boiling at $229.7-230.7^\circ$ (corr.) under 760 mm. pressure; it has a sp. gr. 1.31 at 15° and $K = 0.0094$ at 25° . It forms insoluble zinc, ferrous, and copper salts. Its *silver* salt is an amorphous precipitate. *Methyl methylethylmaleate*, prepared from the silver salt and methyl iodide, is a colourless liquid boiling at 235° . With ammonia in ethereal solution, the anhydride yields the *ammonium* salt of a monoamide, $NH_2 \cdot CO \cdot CMe : CEt \cdot CO_2 \cdot NH_4$, which is a crystalline solid, soluble in water.

The *imide* of methylethylmaleic acid, $\begin{matrix} CMe \cdot CO \\ | \\ CEt - CO \end{matrix} > NH$, is obtained

by heating the anhydride with alcoholic ammonia under pressure at 130° , and forms colourless crystals melting at $66-67^\circ$. This imide is identical with the substance obtained by heating the hæmatic acid, $C_8H_9O_4N$, with alcoholic ammonia at 130° , and yields, on hydrolysis with barium hydroxide, a salt from which methylethylmaleic anhydride can be obtained; the *calcium* salt, $C_7H_8O_4Ca \cdot H_2O$, prepared from the anhydride from the latter source, crystallises in leaflets.

The hæmatic acid, $C_8H_9O_4N$, begins to decompose at 230° , carbon dioxide being evolved and the imide of methylethylmaleic acid formed. When the other hæmatic acid, $C_8H_8O_5$, is heated at 150° , carbon dioxide is evolved and methylethylmaleic anhydride formed.

On oxidising hæmatic acid, $C_8H_8O_5$, with potassium permanganate, succinic acid was alone produced; chromic acid in acetic acid solution also yields succinic acid, the pyruvic acid, which was expected, probably being further oxidised.

On reducing this hæmatic acid, $C_8H_8O_5$, with hydriodic acid, a tri-basic acid, *hæmotricarboxylic acid*, $C_5H_9(CO_2H)_3$, can be isolated, which melts at 145° ; its *silver* salt is an amorphous precipitate, and its *copper* salt a bluish-green precipitate; the *cadmium* salt, $(C_8H_9O_6)_2Cd_3 \cdot 2H_2O$, is a white powder, and the *calcium* salt (with H_2O) a gummy mass. The tribasic acid was also obtained together with an isomeride by reducing the same hæmatic acid by zinc dust and acetic acid, after attempts with sodium and amyl alcohol and sodium amalgam in acid solution had failed; the product of the reduction was separated into two fractions by crystallisation from water; the one, hæmotricarboxylic

acid, melting at 140—141°, forms two-thirds of the reduction product; it crystallises in rosettes of needles and has $K=0.02108$, and the barium and calcium salts crystallise each with H_2O , properties which show it to be identical with the hæmotricarboxylic acid (m. p. 145°) obtained by reduction with hydriodic acid; the *methyl* ester was prepared from the silver salt and is a yellow oil boiling at 293°. All attempts to obtain an anhydride from this tricarboxylic acid failed.

The less fusible isomeride, the hæmotricarboxylic acid melting at 175—176°, crystallises in needles and has $K=0.2274$; its *barium* salt, $(C_8H_9O_6)_2Ba_3 \cdot H_2O$, and its other salts resemble those of the isomeride (m. p. 140°). Attempts to prepare an anhydride led to the complete conversion of the acid into the isomeride. This isomeric change is also effected by heating the acid (with the higher melting point) with water or hydrochloric acid under pressure at 200°. The reverse change could not be brought about. This behaviour is in agreement with the view that the pentenetricarboxylic acid is a derivative of maleic acid,

thus:
$$\begin{array}{c} CH_3 \cdot C \cdot CO_2H \\ | \\ CO_2H \cdot CH_2 \cdot CH_2 \cdot C \cdot CO_2H \end{array}$$
 In the reduction, two asymmetric carbon atoms are produced, and thus two inactive hæmotricarboxylic acids exist.

The reduction of the hæmatic acid, $C_8H_9O_4N$, by hydrogen iodide and phosphonium iodide seems to lead only to the production of a mixture of the two stereoisomeric hæmotricarboxylic acids. When zinc dust and acetic acid were used, no definite results were obtained, partial hydrolysis of the imide, as well as reduction, having taken place. An impure *imide*, $C_8H_{11}O_4N$, was obtained and melted at 80—83°; the calcium salt, $(C_8H_{10}O_4N)_2Ca \cdot 2H_2O$, was analysed. When hydrolysed with 50 per cent. sulphuric acid, a mixture of the two isomeric hæmotricarboxylic acids was obtained.

Attempts were made to reduce methylethylmaleic anhydride, using in the first place hydriodic acid and then zinc dust and acetic acid, aluminium amalgam in sulphuric acid solution, and finally sodium amalgam in alkaline solution. In all cases except the last, a small yield of the fumaroid form of methylethylsuccinic acid (m. p. 172—173°) was obtained.

K. J. P. O.

Constitution of Platinum Bases. SOFUS M. JÖRGENSEN (*Zeit. anorg. Chem.*, 1906, **48**, 374—388. Compare Abstr., 1900, i, 542; 1901, i, 163).—When the ethylenediamine salt of Zeise's acid is treated with several times its weight of cold water, hydrogen chloride is eliminated and a new compound, *s-platoethylenediamine-ethylene chloride*, separates in very small, yellow crystals according to the equation:

$$C_2H_4N_2 \cdot H_6(Cl_2PtC_2H_4Cl)_2 = C_2H_4(ClNH_2PtC_2H_4Cl)_2 + 2HCl$$
; the reaction is a reversible one. Two other methods for the preparation of this compound are given. When, on the other hand, the ethylenediamine salt of Zeise's acid is heated in aqueous solution, a substance, already described by Griess and Martius (*Annalen*, 1861, **120**, 225), separates in yellow needles; the author shows that this compound is *s-platoethylenediamine chloride*, $C_2H_4(ClNH_2)_2Pt$, previously obtained by him by other methods (*loc. cit.*).

The second part of the paper deals with the question as to which of the two formulæ, $\text{ClNH}_2\text{PtNH}_3\text{Cl}$ and $\text{ClPtNH}_2\text{NH}_3\text{Cl}$, pertains to the chloride first described by Peyrone, and which to Reiset's so-called second chloride. The author, in a former paper, has contended that, contrary to the view of Cleve and Blomstrand, the symmetrical constitution is to be ascribed to Peyrone's chloride and considers that he has now decided the question in his favour by showing that the compound of Peyrone's chloride with dimethylamine is isomeric and not identical with the compound which ammonia forms with the dimethylamine compound corresponding with Peyrone's chloride; only the chloride with a symmetrical constitution can give isomerides in these circumstances.

Dimethylamine platinochloride, $\text{Pt}[(\text{CH}_3)_2\text{NH}]_2\text{Cl}_2$, already described by Koefoed, was obtained by interaction of potassium platinochloride and dimethylamine in aqueous solution, and occurs in rhombic plates. The structure of this compound is similar to that of Peyrone's salt, since the pyridine compound corresponding with the latter gives the same compound with dimethylamine as Koefoed's salt by interaction with pyridine in aqueous solution. Further, the mixed dimethylamine ammonia salts, obtained by interaction of Peyrone's salt with dimethylamine and of Koefoed's salt with ammonia, although distinct (see later), yield the same products when heated with hydrochloric acid. Koefoed's salt dissolves slowly in cold aqueous dimethylamine, and from the solution a compound was isolated which with ammonia yielded a platodiammine different from that obtained by the action of ammonia on Koefoed's salt, but identical with the salt obtained by the action of dimethylamine on Reiset's chloride, a further proof that Koefoed's salt corresponds in constitution with Peyrone's salt.

The mixed *platodiammine* salt, $\text{Pt}\{(\text{NH}_3)_2[(\text{CH}_3)_2\text{NH}]_2\}\text{Cl}_2$, obtained by the action of ammonia on Koefoed's salt, forms colourless, crystalline masses; the isomeric compound obtained by interaction of Peyrone's chloride and dimethylamine forms large, clear plates. As these compounds readily change the one into the other, their double salts with platinous chloride, obtained by interaction of the respective compounds with potassium platinochloride in acidified aqueous solution, have been investigated. The double salt obtained from the compound first mentioned occurs in light yellow, anhydrous needles, which are not dichroic; the isomeric salt forms red dichroic needles which crystallise with $1\text{H}_2\text{O}$. It is shown by solubility determinations at the ordinary temperature that these double salts are distinct substances.

G. S.

The Precipitability of Amino-acids by Phosphotungstic Acid. PHOEBUS A. LEVENE and W. BEATTY (*Zeit. physiol. Chem.*, 1906, 47, 149—150).—As a rule, amino-acids are precipitable only from concentrated solutions by a concentrated solution of phosphotungstic acid. Particulars in relation to the following amino-acids are given: glycine, alanine, leucine, phenylalanine, and glutamic acid.

W. D. H.

Amine Derivatives of Mesoxalic Esters. RICHARD S. CURTISS (*Amer. Chem. J.*, 1906, 35, 354—358).—*Ethyl dihydroxyiminodi-*

malonate, $\text{NH}[\text{C}(\text{OH})(\text{CO}_2\text{Et})_2]_2$, prepared by the action of dry ammonia on a well-cooled solution of ethyl dihydroxymalonate in benzene in presence of zinc chloride, crystallises from ether in flat, rectangular tablets, melts at $103-105^\circ$, decomposes at $105-110^\circ$ with evolution of ammonia, is soluble in benzene, ethyl acetate, acetone, or chloroform, and is rapidly decomposed by water. This compound can also be obtained by the action of ammonia on ethyl oxomalonate.

E. G.

Derivatives of Formhydroxamic Acid and the Possible Existence of Esters of Fulminic Acid. II. HENRY C. BIDDLE (*Amer. Chem. J.*, 1906, **35**, 346—353).—In an earlier paper (*Abstr.*, 1905, i, 181), it was shown that when methyl chloroformoxime is treated with potassium hydroxide, a compound is produced which, it was suggested, might be methyl fulminate. A further study of the reaction has proved that the substance is not methyl fulminate, but is methyl di-imino-oxalate which has been synthesised by the following method.

By the action of chlorine on a solution of potassium cyanide in methyl alcohol diluted with water, a mixture of methyl cyanoiminocarbonate and methyl di-imino-oxalate is produced. *Methyl cyanoiminocarbonate*, $\text{NH}:\text{C}(\text{OMe})\cdot\text{CN}$, is a colourless, mobile liquid, which boils at $33-34^\circ$ under 22 mm. pressure, has a peculiar, isonitrile-like odour, is slightly soluble in water, and is somewhat unstable. *Methyl di-imino-oxalate*, $\text{NH}:\text{C}(\text{OMe})\cdot\text{C}(\text{OMe})\cdot\text{NH}$, crystallises in colourless, transparent plates, has a peculiar, sweet odour, and is more stable than methyl cyanoiminocarbonate, although it gradually changes into a dark resin. When the ester is treated with dilute hydrochloric acid, it is converted into ammonia and methyl oxalate.

E. G.

Preparation of Acetamide. MAURICE FRANÇOIS (*J. Pharm. Chim.*, 1906, [vi], **23**, 230—237).—When ammonium acetate is heated, it decomposes, producing ammonia and ammonium hydrogen acetate; the latter on further heating yields water, acetic acid, and acetamide. The ordinary laboratory process of preparing acetamide by distilling ammonium acetate therefore gives a poor yield not exceeding 28 per cent. of the theoretical. By starting with ammonium hydrogen acetate, a yield of acetamide equivalent to 45.3 per cent. of the theoretical can be obtained. The special apparatus employed by the author in distilling the diacetate is figured in the original.

T. A. H.

Dialkylmalonamides. KARL BÖTTCHER (*Chem. Zeit.*, 1906, **25**, 272).—In opposition to Meyer (this vol., i, 138), the author finds that methylethylmalonyl chloride reacts with concentrated aqueous ammonia to give a 90 per cent. yield of the corresponding diamide, and not methylethylacetamide, as stated by Meyer.

P. H.

Mercuric Oxycyanide. ERWIN RUPP (*Arch. Pharm.*, 1906, **244**, 1—2).—The abnormal character of mercuric oxycyanide, $\text{Hg}(\text{CN})_2\cdot\text{HgO}$, may be explained by regarding it as a complex salt with the ions $\cdot\text{Hg}\cdot\text{O}\cdot\text{Hg}\cdot$ and $2\cdot\text{CN}\cdot$.

C. F. B.

Hydrargyrum Oxycyanatum. VON PIEVERLING (*Arch. Pharm.*, 1906, 244, 35—36).—The pastilles of this substance no longer contain sodium chloride.

Mercuric oxycyanide does not equal the cyanide in its power of killing bacteria; it is its power of preventing their development which is remarkable. C. F. B.

Arsonic and Arsinic Acids. WILLIAM M. DEHN and S. J. McGRATH (*J. Amer. Chem. Soc.*, 1906, 28, 347—361).—The arsonic and arsinic acids are white, crystalline substances which are soluble in water or alcohol, but insoluble in ether.

Magnesium n-propylarsonate, $\text{MgAsPr}^{\text{a}}\text{O}_3$, prepared in the same manner as the ethylarsonate (Abstr., 1905, i, 184), forms pearly-white, soapy crystals containing $\frac{1}{2}\text{H}_2\text{O}$. When this salt is treated with the calculated quantity of strong sulphuric acid and the product is extracted with alcohol, *n-propylarsonic acid*, $\text{AsPr}^{\text{a}}\text{O}(\text{OH})_2$, is obtained, which crystallises in needles and melts at 125° ; an aqueous solution, saturated at 26° , contains 43 per cent. of the acid. When a solution of the magnesium salt in dilute hydrochloric acid is treated with hydrogen sulphide, *n-propylarsine disulphide*, $\text{Pr}^{\text{a}}\text{AsS}_2$, is obtained as a light yellow, viscid oil which has a sp. gr. 1.8 and, when cooled below -10° , becomes a gummy mass.

isoAmylarsonic acid, $\text{C}_5\text{H}_{11}\cdot\text{AsO}(\text{OH})_2$, forms pearly-white crystals, melts at 194° , is soluble in water at 28° to the extent of 0.82 gram in 100 c.c. and in alcohol at 21° to the extent of 2.2 grams in 100 c.c. *isoAmylarsine disulphide*, $\text{C}_5\text{H}_{11}\cdot\text{AsS}_2$, is a viscid, light yellow oil, which cannot be distilled without decomposition.

Benzylarsonic acid, $\text{CH}_2\text{Ph}\cdot\text{AsO}(\text{OH})_2$, crystallises in long, white, lustrous needles, has a bitter taste, melts at 167° , and is stable in the air; 100 c.c. of an aqueous solution, saturated at 22.5° , contain 0.34 gram; at 27° , 0.39 gram; and at 97° , 3.50 grams of the acid; a saturated alcoholic solution at 23° contains 0.87 gram, and at 70° , 5.91 grams of the acid in 100 c.c. *Benzylarsine disulphide* is a heavy, bright yellow oil which, on heating, decomposes with evolution of hydrogen sulphide and formation of arsenious oxide and stilbene. When benzylarsonic acid is heated, it undergoes decomposition with production of benzyl alcohol, benzaldehyde, stilbene, arsenious oxide, and water. The acid is decomposed by concentrated hydrochloric acid with formation of benzyl chloride and arsenious acid, and more rapidly by sulphuric acid with formation of dibenzyl, benzaldehyde, and arsenious acid.

Magnesium ethylarsonate is decomposed by heat into magnesium oxide, metallic arsenic, methane, ethylene, and water. When magnesium *n*-propylarsonate is heated, it yields a gaseous mixture consisting of hydrogen, methane, ethylene, and propylene.

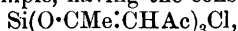
Determinations have been made of the rate of transformation of potassium arsenite into arsonic acids at 25° when treated with *isobutyl* iodide, chloroform, bromoform, iodoform, *p*-chlorotoluene, and allyl iodide; the results are tabulated.

The following solubilities have been determined, the quantity in each case being the number of grams of the substance contained in

100 c.c. of the solution saturated at the given temperature. Ethylarsonic acid in water at 27°, 70.00; at 40°, 112.00; and in alcohol at 25°, 39.40. Phenylarsonic acid in water at 28°, 3.25; at 41°, 4.82; at 52°, 8.52; and at 84°, 24.0; in alcohol at 26°, 15.51, and at 68°, 55.40. Methylarsinic acid in water at 22°, 82.90. Phenylarsinic acid in water at 27°, 0.28; in alcohol at 22°, 11.80, and at 55°, 57.70.

Ethylarsonic acid melts at 99.5°, phenylarsonic acid at 158.0°, and phenylarsinic acid at 164.0°. E. G.

Siliconium, Boronium, and Titanonium Salts. WALTHER DILTHEY [and, in part, F. EDUARDOFF and F. J. SCHUMACHER] (*Annalen*, 1906, 344, 300—342. Compare Abstr., 1903, i, 405, 591; 1904, i, 132, 290; Dilthey and Eduardoff, Abstr., 1904, i, 464; this vol., i, 128; Werner, Abstr., 1902, ii, 554; Baeyer, Abstr., 1905, i, 281).—Siliconium, boronium, and titanonium chlorides are formed by the action of silicon tetrachloride, boron trichloride, and titanium tetrachloride respectively on α -diketones. The chlorides can be converted into bromides, iodides, periodides, nitrates, and sulphates, and yield additive compounds with metallic salts. In these "onium" salts, the metalloid atom must be attached to oxygen, the derivatives of acetylacetone, for example, having the constitutions



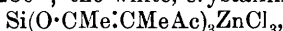
$\text{Ti}(\text{O} \cdot \text{CMe} \cdot \text{CHAc})_3\text{Cl}$, and $\text{B}(\text{O} \cdot \text{CMe} \cdot \text{CHAc})_2\text{Cl}$, respectively, as they are formed the more easily the more stable is the enolic form of the diketone, and are readily hydrolysed by water or moist air, whilst compounds such as triphenylsilicon chloride and phenylboron dichloride, in which the metalloid atom is attached directly to carbon, are stable towards water. The siliconium salts resemble trimethoxysilicon chloride, $\text{Si}(\text{OMe})_3\text{Cl}$, but whilst the chlorine atom of the latter can be substituted by alkyl groups, the chlorine atom of the siliconium chlorides cannot be substituted by alkyl groups or by diketones, and the compound has the character of a salt. This difference in the function of the chlorine atom is explained by means of Werner's co-ordination theory.

Triacetylacetonysiliconium zincchloride, $\text{Si}(\text{O} \cdot \text{CMe} \cdot \text{CHAc})_2\text{ZnCl}_3$, forms white needles and becomes brown at about 240°, but does not melt at 300°. The *iodide*, $\text{Si}(\text{O} \cdot \text{CMe} \cdot \text{CHAc})_3\text{I}$, formed by the action of hydrogen iodide on the chloride in glacial acetic acid solution, crystallises in glistening, white needles; the *periodide*, $\text{Si}(\text{O} \cdot \text{CMe} \cdot \text{CHAc})_3\text{I}_3$, crystallises in violet needles; the *picrate* forms yellow needles and decomposes slowly on exposure to air.

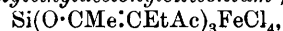
Triacetylacetonysiliconium ferrichloride,



forms long, pointed, greenish-yellow leaflets and melts at 210°; the unstable *aurichloride*, $\text{Si}(\text{O} \cdot \text{CMe} \cdot \text{CMeAc})_3\text{AuCl}_4$, crystallises in slender, golden-yellow needles and melts and decomposes at 206°; the *platnichloride*, $[\text{Si}(\text{O} \cdot \text{CMe} \cdot \text{CMeAc})_3]_2\text{PtCl}_6$, forms yellow needles and commences to blacken at 280°; the white, crystalline *zincchloride*,



melts at 220°. *Triacetylacetonysiliconium ferrichloride*,

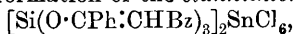


crystallises in yellow needles and melts at 157°; the *aurichloride*, $\text{Si}(\text{O} \cdot \text{CMe} \cdot \text{CEtAc})_3\text{AuCl}_4$, forms golden-yellow needles and melts at

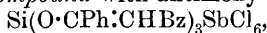
148°; the *platinichloride*, $[\text{Si}(\text{O}\cdot\text{CMe}\cdot\text{CEtAc})_3]_2\text{PtCl}_6$, crystallises in orange prisms, and decomposes but does not melt below 300°; the *periodide*, $\text{Si}(\text{O}\cdot\text{CMe}\cdot\text{CEtAc})_3\text{I}_3$, crystallises in violet prisms.

The *tribenzoylacetonysiliconium platinichlorides* formed from the isomeric ferrichlorides are obtained as long, slender, yellow needles and nodular aggregates of orange-yellow crystals respectively; the two preparations are equally insoluble, and decompose without melting at about 200°

Tridibenzoylmethylsiliconium zincochloride, $[\text{Si}(\text{O}\cdot\text{CPh}\cdot\text{CHBz})_3]_2\text{ZnCl}_4$, formed by the action of zinc chloride on tridibenzoylmethylsiliconium chloride in glacial acetic acid solution, crystallises in sheaves of white needles and is only slowly decomposed by aqueous sodium carbonate. The action of stannic chloride ($\frac{1}{2}$ mol.) on the chloride in chloroform solution leads to the formation of the *stannichloride*,



which separates in stout crystals, is insoluble in most solvents, but dissolves in ethylene dibromide and melts above 305°, at which temperature it is only slightly decomposed. It dissolves in a chloroform solution of stannic chloride, from which, on addition of glacial acetic acid, the *stannichloride*, $\text{Si}(\text{O}\cdot\text{CPh}\cdot\text{CHBz})_3\text{SnCl}_5$, separates in yellow needles; this melts when quickly heated at 290–291°, is readily soluble in chloroform, and when left in contact with a mixture of chloroform and glacial acetic acid is reconverted into the normal stannichloride. The compound with antimony pentachloride,



separates from glacial acetic acid in yellow crystals and is readily soluble in chloroform.

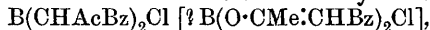
The compound of silicon tetrachloride with ethyl acetoacetate (Rosenheim, Loewenstamm, and Singer, *Abstr.*, 1903, i, 603) is much less stable than triacetylacetonysiliconium chloride, as it is decomposed by ferric chloride in glacial acetic acid solution. The crystalline *ferrichloride*, $\text{Si}(\text{O}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et})_3\text{FeCl}_4$, formed in chloroform solution, is unstable. Ethyl benzoylacetate reacts with silicon tetrachloride only with difficulty, whilst ethyl malonate does not form siliconium salts.

In the absence of a solvent, silicochloroform and acetylacetone interact with explosive violence, but in the presence of much chloroform the interaction leads to the formation of triacetylacetonysiliconium chloride hydrochloride, hydrogen chloride, and hydrogen; the same siliconium compound is formed by the interaction of phenylsilicon trichloride and acetylacetone.

The methods of preparation, the properties, and the reactions of the boronium salts are similar to those of the siliconium salts, the two groups differing chiefly in their stability. The compound formed by the action of acetylacetone on boron trichloride in ethereal solution, $\text{B}(\text{CO}\cdot\text{CMe}\cdot\text{HAc})_2\text{Cl}$ or $\text{B}(\text{O}\cdot\text{CMe}\cdot\text{CHAc})_2\text{Cl}\cdot\text{HCl}$, is extremely unstable. The *ferrichloride*, BR_2FeCl_4 , crystallises in lemon-yellow leaflets and melts and decomposes at 137°; the *aurichloride*, BR_2AuCl_4 , crystallises from a mixture of chloroform and ether in leaflets and melts at 135°; the *platinichloride*, $(\text{BR}_2)_2\text{PtCl}_6$, forms large, reddish-yellow crystals and blackens at about 180°, but does not melt at 300°; the *iodide*, BR_2I , forms unstable, yellow crystals; the *periodide*

BR_2I_3 , separates in glistening, stout, reddish-brown crystals; the crystalline *sulphate* is deliquescent; the *zincchloride*, BR_2ZnCl_3 , forms coarse, white crystals and melts and decomposes at 206° ; the *stannichloride*, BR_2SnCl_3 , crystallises in slender, white prisms and melts at $210\text{--}212^\circ$.

The compound of boron trichloride with benzoylacetone,



or its *hydrochloride* is obtained as an unstable, yellowish-white substance which is readily soluble in glacial acetic acid or chloroform. The *ferrichloride*, $\text{B}(\text{CHAcBz})_2\text{FeCl}_4$, forms nodular aggregates of stout, yellow crystals and slender, yellow needles, the latter form only being obtained on recrystallisation of the salt from chloroform; it melts at $180\text{--}182^\circ$; the *platinichloride* is stable and insoluble; the *zincchloride*, $\text{B}(\text{CHAcBz})_2\text{ZnCl}_3$, is obtained in stout plates melting at 208° and in long needles melting at about 220° ; when recrystallised from hot glacial acetic acid, both forms yield colourless needles melting at $223\text{--}225^\circ$; the *iodide*, $\text{B}(\text{CHAcBz})_2\text{I}$, is obtained as a reddish-yellow powder, which appears under the microscope as a mixture of a yellow with a violet-brown substance, and on recrystallisation from chloroform forms yellow crystals melting at 210° ; the *periodide*, $\text{B}(\text{CHAcBz})_2\text{I}_3$, forms violet-brown, glistening prisms with green lustre; the *stannichloride*, $[\text{B}(\text{CHAcBz})_2]_2\text{SnCl}_6$, was analysed.

The action of boron trichloride on dibenzoylmethane in ethereal solution leads to the formation of an extremely unstable, white, crystalline product which loses hydrogen chloride when dried.

Titanium tetrachloride and acetylmethylacetone interact in glacial acetic acid solution, forming the compound $[\text{Ti}(\text{O}\cdot\text{CMe}\cdot\text{CMeAc})_3]_2\cdot\text{TiCl}_6$, which separates in yellowish-red crystals and decomposes slowly on exposure to moist air. The *ferrichloride*, $\text{Ti}(\text{O}\cdot\text{CMe}\cdot\text{CMeAc})_3\text{FeCl}_4$, formed by the action of titanium tetrachloride on a glacial acetic acid solution of acetylmethylacetone and anhydrous ferric chloride, is obtained as a brownish-red, crystalline product, soluble in ethyl acetate or hot glacial acetic acid.

The red *product*, $[\text{Ti}(\text{CHAcBz})_3]_2\cdot\text{TiCl}_6$, formed by the interaction of titanium tetrachloride and benzoylacetone, is only moderately stable.

The unstable, dark red, crystalline *product*, $[\text{Ti}(\text{O}\cdot\text{CPh}\cdot\text{CHBz})_3]_2\cdot\text{TiCl}_6$, was analysed.

Salicylaldehyde interacts with titanium tetrachloride in the same manner as the $\alpha\gamma$ -diketones, forming an unstable titanonium salt. The *product* of the interaction of ethyl salicylate and titanium tetrachloride crystallises in yellowish-red needles and deliquesces immediately on exposure to air. *o*-Hydroxyacetophenone and *o*-hydroxybenzophenone yield similar red, unstable *titanonium* salts.

Stannic chloride interacts with acetylacetone or its copper derivative in chloroform solution, forming the *product* $\text{Sn}(\text{O}\cdot\text{CMe}\cdot\text{CHAc})_2\text{Cl}_2$, which melts at 203° and is decomposed by ferric chloride or hydrogen iodide, yielding in the latter case stannic iodide. Stannic bromide interacts with $\alpha\gamma$ -diketones in the same manner as the chloride.

The product of the interaction of antimony pentachloride and acetylacetone (compare Rosenheim, Loewenstamm, and Singer, *loc. cit.*) has the molecular formula $\text{Sb}(\text{O}\cdot\text{CMe}\cdot\text{CHAc})\text{Cl}_4$, crystallises in yellow plates or

leaflets, melts at 137° , and is decomposed by ferric chloride or hydrogen iodide. Antimony pentachloride interacts with other diketones such as dibenzoylmethane to form yellow substitution products.

G. Y.

Nitration of *o*- and *m*-Dibromobenzenes. ARNOLD F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 8, 678—680. Compare Abstr., 1905, i, 41, 42).—*m*-Dibromobenzene, prepared from pure *m*-bromoaniline, solidifies at -7° and has the sp. gr. 1.960 at 18.5° . *o*-Dibromobenzene, prepared from *o*-bromoaniline, solidifies at 6° and has the sp. gr. 1.996 at 11° . The six dibromonitrobenzenes have been prepared in the same way as the dichloronitrobenzenes (*loc. cit.*). The composition of the products of nitration at 0° were determined from their solidifying points and their sp. gr. Whilst *o*-dichlorobenzene yields 7.2 per cent., and *m*-dichlorobenzene 4.0 per cent., *o*-dibromobenzene yields 18.3 per cent., and *m*-dibromobenzene 4.6 per cent. of the by-product.

G. Y.

Introduction of Halogen Atoms into the Benzene Nucleus during the Reduction of Aromatic Nitro-compounds. JAN J. BLANKSMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 8, 680—683. Compare Abstr., 1905, i, 761; Goldschmidt and Ingebrechtsen, Abstr., 1904, ii, 608).—If 10 c.c. of nitrobenzene are boiled with 100 c.c. of alcohol and 200 c.c. of 25 per cent. hydrochloric acid in a reflux apparatus, and 15 grams of tin are added gradually in small portions, the reduction product consists of 55 per cent. of *o*- and *p*-chloroanilines, together with 45 per cent. of aniline. If the nitrobenzene is reduced slowly with stannous chloride and hydrochloric acid, 53 per cent. of the product consists of *o*- and *p*-chloroanilines. Similar results are obtained with nitrobenzene.

The slow reduction of nitrobenzene with tin and hydrobromic acid leads to the formation of a mixture of aniline and *o*- and *p*-bromoanilines.

The formation of the *o*- and *p*-chloro- and bromo-anilines must be in consequence of the intermediate production of phenylhydroxylamine.

G. Y.

New Aromatic Hydrocarbons. DANIEL VORLÄNDER and CARL SIEBERT (*Ber.*, 1906, 39, 1024—1035).—*Tetraphenylallene*, $\text{CPh}_2:\text{C}:\text{CPh}_2$, is obtained when dry barium diphenylacetate is distilled under a pressure of 15—20 mm., the distillate freed from oil, and the solid product crystallised from hot acetone. It forms colourless needles or prisms, melts at 164 — 165° , and dissolves readily in most organic solvents with the exception of cold alcohol and light petroleum. When moistened with concentrated sulphuric acid, it becomes deep violet-brown, and dissolves to a greenish-violet-brown solution, which gradually changes to orange; similar changes in colour are observed with solutions of hydrogen chloride or bromide in glacial acetic acid, and are due to the formation of a new hydrocarbon which melts at 135° . Tetraphenylallene forms unstable, dark-coloured additive compounds with halogen hydracids at low temperatures, but does not combine with picric acid. It does not react with a boiling 20 per cent.

solution of potassium hydroxide, sodium ethoxide, acetic anhydride, alcoholic ammonia, phenylhydrazine, or boiling aniline, and does not combine with ethyl sodiomalonate or magnesium phenyl bromide. When reduced with red phosphorus and hydriodic acid in acetic acid solution, or with sodium and boiling alcohol, it yields *s*-tetraphenylpropane, $C_{27}H_{24}$, which crystallises from alcohol in needles melting at 139° . Oxidation with chromic acid in acetic acid solution converts the unsaturated hydrocarbon into benzophenone. When the oxidation is less vigorous, a *product* melting at 195 — 197° is obtained.

Tetraphenylallene is readily converted into an isomeric *hydrocarbon* $C_{27}H_{20}$, probably $C_6H_4 \begin{smallmatrix} \text{CPh} \\ \diagup \quad \diagdown \\ \text{CPh}_2 \end{smallmatrix} CH$, when its acetic acid solution is saturated with hydrogen chloride, kept until it becomes colourless, and then poured into water. The hydrocarbon crystallises from methyl alcohol in colourless prisms, melts at 134 — 135° , is somewhat more readily soluble than its isomeride, and its solution in concentrated sulphuric acid has an orange-yellow colour. When brominated in chloroform solution, it yields a *monobromo*-derivative, $C_{27}H_{19}Br$, which crystallises from alcohol in flat needles melting at 167 — 168° . It is extremely stable, and the bromine is not removed by boiling with aqueous or alcoholic potassium hydroxide or by heating with lead oxide and acetic acid. It does not give a coloration with cold concentrated sulphuric acid, but when warmed an intense magenta-red coloration is developed. The same bromo-derivative is obtained by the action of bromine on tetraphenylallene.

When reduced, the new hydrocarbon yields a *product*, $C_{27}H_{22}$, melting at 113 — 114° , and, when oxidised, a neutral *product* melting at 146 — 148° .

Considerable quantities of diphenylmethane and small amounts of a *hydrocarbon* (mol. wt. about 320) which crystallises from aqueous alcohol in colourless needles melting at 121° are also formed when barium diphenylacetate is distilled. Hot hydrochloric acid transforms this hydrocarbon into an isomeride melting at 104° . Both compounds yield benzophenone when oxidised.

Tetraphenylallene has been synthesised by the following methods:
 A. *Tetraphenylpropylene*, $CHPh_2 \cdot CH : CPh_2$, is readily formed when Kohler's $\alpha\alpha\gamma$ -tetraphenylpropyl alcohol, diphenylethyldiphenylcarbinol (Abstr., 1904, i, 596), is boiled with acetic anhydride or 20 per cent. hydrochloric acid. It crystallises from alcohol in plates, melts at 127 — 128° , dissolves readily in benzene, chloroform, or acetone, and when reduced yields tetraphenylpropane. When suspended in chloroform and brominated, it yields *tetraphenylbromopropylene*, $C_{27}H_{21}Br$, melting at 124° , and this, with alcoholic potash, yields tetraphenylallene.
 B. [With J. OSTERBURG.] Kohler and Johnston's phenylbenzylideneacetophenone (Abstr., 1905, i, 215) reacts with an excess of magnesium phenyl bromide in ethereal solution, and the product, after treatment with dilute hydrochloric acid, yields $\alpha\alpha\gamma$ -tetraphenylpropylene alcohol, $CPh_2 \cdot CH \cdot CPh_2 \cdot OH$, which crystallises from alcohol in prisms melting at 138 — 139° . Its behaviour towards most reagents is similar to that of the allene derivative, and when boiled with acetic anhydride it is transformed into tetraphenylallene. J. J. S.

Molecular Compounds of Nitro-derivatives with Amines. ROBERT KREMANN (*Ber.*, 1906, 39, 1022—1024. Compare Noelting and Sommerhoff, this vol., i, 157).—The non-isolation of a definite additive compound cannot be regarded as direct evidence that the components cannot form such a compound. The only method for proving the non-existence of such compounds is the examination of the melting-point diagram as previously described (*Abstr.*, 1905, ii, 76, 77). It is pointed out that meta- and para-disubstituted derivatives of benzene form additive compounds more readily than ortho derivatives. J. J. S.

Condensation Products of Organic Bases with ψ -Phenols containing Strongly Negative Substituting Groups. KARL AUWERS and OTTO SCHRÖTER (*Annalen*, 1906, 344, 257—270. Compare this vol., i, 259).—The *methylamine* derivative of α -5-dibromo-6-hydroxy-3-methylbenzaldehyde, $\text{NMe} \cdot \left(\text{CH}_2 \cdot \text{C} \begin{array}{l} \swarrow \text{CH} : \text{C}(\text{CHO}) \\ \searrow \text{CH} \text{---} \text{CBr} \end{array} \text{C} \cdot \text{OH} \right)_2$, formed by the action of aqueous methylamine on the ψ -phenol in concentrated benzene solution, is yellow, melts at 136—141°, is insoluble or only sparingly soluble in organic solvents, remains unchanged on prolonged heating on the water-bath, and is stable towards hot 5 per cent. aqueous sodium hydroxide or cold glacial acetic acid. When heated with glacial acetic acid, it is decomposed, forming the monoacetate of 5-bromo- α -6-dihydroxy-3-methylbenzaldehyde, melting at 102° (Auwers and Huber, *Abstr.*, 1902, i, 213). When boiled with acetic anhydride the methylamine derivative yields the *diacetate*, $\text{OAc} \cdot \text{C}_6\text{H}_2\text{Br}(\text{CHO}) \cdot \text{CH}_2 \cdot \text{OAc}$, which crystallises in stellate groups of needles and melts at 74—75°.

The *diethylamine* derivative, $\text{NEt}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_2\text{Br}(\text{CHO}) \cdot \text{OH}$, crystallises from methyl alcohol in colourless plates and prisms and melts and becomes red at 146—147°, but when heated on the water-bath or boiled with 5 per cent. sodium hydroxide remains unchanged. When treated with cold glacial acetic acid, it is decomposed, yielding a small amount of a product, $\text{CH}_2[\text{C}_6\text{H}_2\text{Br}(\text{CHO}) \cdot \text{OH}]_2$ (?), which melts at about 187°. The diethylamine derivative yields the monoacetate melting at 102° when boiled with glacial acetic acid, and a non-nitrogenous *product* when boiled with acetic anhydride. The *diamylamine* derivative, $\text{N}(\text{C}_5\text{H}_{11})_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_2\text{Br}(\text{CHO}) \cdot \text{OH}$, crystallises in colourless leaflets, melts at 72—74°, is readily soluble in chloroform, benzene, or acetone, and decomposes extremely slowly when heated on the water-bath, but remains unchanged when boiled with dilute sodium hydroxide. It shows the same behaviour towards cold and hot glacial acetic acid as the methylamine derivative, but forms the monoacetate melting at 102° when boiled with acetic anhydride.

The *methylaniline* derivative, $\text{NMePh} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_2\text{Br}(\text{CHO}) \cdot \text{OH}$, crystallises from benzene, melts at 116—117°, and remains unchanged when boiled with dilute alkali hydroxides. The *pyridine* compound, $\text{OH} \cdot \text{C}_6\text{H}_3(\text{CHO}) \cdot \text{CH}_2 \cdot \text{C}_5\text{NH}_5\text{Br} [\text{OH} : \text{CHO} : \text{CH}_2 = 6 : 1 : 3]$, is obtained as a white powder and melts at 188—190°.

3-Bromo-5-nitro-4-hydroxybenzyl bromide, $\text{OH} \cdot \text{C}_6\text{H}_2\text{Br}(\text{NO}_2) \cdot \text{CH}_2\text{Br}$,

formed by bromination of Stoermer and Behn's *m*-nitro-*p*-hydroxybenzyl alcohol (Abstr., 1901, i, 726) in hot glacial acetic acid solution, crystallises from petroleum in sheaves of long, slender, yellow needles, melts at 89—90°, is soluble in cold benzene, chloroform, or acetone, and loses hydrogen bromide when treated with alcohol or aqueous acetone. The *monoacetate*, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)\cdot\text{CH}_2\cdot\text{OAc}$, formed by boiling the benzyl bromide with sodium acetate in glacial acetic acid solution, crystallises in small, glistening, yellow prisms and plates, melts at 112—113°, and is converted by boiling acetic anhydride into the *diacetate*, $\text{OAc}\cdot\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)\cdot\text{CH}_2\cdot\text{OAc}$, which forms colourless, glistening needles and melts at 58—59°. The *methylamine* derivative, $\text{NMe}[\text{CH}_2\cdot\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)\cdot\text{OH}]_2$, is orange-red, melts at 184—185°, and remains unchanged when heated on the water-bath, boiled with aqueous sodium hydroxide, or treated with cold glacial acetic acid. It is only slightly decomposed, yielding traces of methylamine when boiled with glacial acetic acid, and when heated with acetic anhydride forms an *acetyl* derivative which melts at 156° and on hydrolysis yields the methylamine derivative.

The *diethylamine* derivative, $\text{NEt}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)\cdot\text{OH}$, crystallises in orange-yellow prisms or long, thin leaflets, melts at 164—165°, is readily soluble in acetone, but more sparingly so in benzene or methyl or ethyl alcohol, and remains unchanged when heated on the water-bath or treated with glacial acetic acid, but is partially resinified when boiled with aqueous alkali hydroxides. It forms the monoacetate melting at 112—113° when boiled with glacial acetic acid, and yields diethylamine when heated with acetic anhydride.

The *diamylamine* derivative, $\text{N}(\text{C}_5\text{H}_{11})_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)\cdot\text{OH}$, crystallises in glistening, orange-yellow leaflets, melts at 129—129.5°, and remains unchanged when heated on the water-bath, boiled with alcoholic-aqueous sodium hydroxide, or treated with cold glacial acetic acid. It yields the monoacetate melting at 112—113°, and the diacetate melting at 58—59°, when boiled with glacial acetic acid and acetic anhydride respectively.

G. Y.

Certain Derivatives of Phenylglycine-*o*-sulphonic Acid.

HAMILTON BRADSHAW (*Amer. Chem. J.*, 1906, 35, 340—346).—*Phenylglycine-*o*-sulphonic acid*, $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, obtained by the action of formaldehyde and hydrogen cyanide on aniline-*o*-sulphonic acid, is a crystalline substance; its *potassium hydrogen* salt is sparingly soluble in cold water. *p*-*Bromophenylglycine-*o*-sulphonic acid*, obtained in a similar manner, forms flaky crystals, is very soluble in water, and yields a methyl ester; its *potassium hydrogen* salt crystallises in needles.

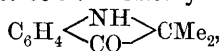
Attempts were made to effect condensations of *p*-bromophenylglycine-*o*-sulphonic acid with production of substances analogous to indigo, but without success. When potassium *p*-bromophenylglycine-*o*-sulphonate was treated with fuming sulphuric acid, it was decomposed with formation of *p*-bromoaniline-*o*-sulphonic acid. By the action of acetic anhydride on the potassium salt, a soluble product was obtained which was probably a sulphonic acid in which acetylation had taken place in the imino-group. Attempts to prepare a normal ester of

p-bromophenylglycine-*o*-sulphonic acid by the action of methyl iodide were unsuccessful. When potassium hydrogen *p*-bromophenylglycine-*o*-sulphonate was heated with sodamide, no condensation product could be obtained. E. G.

Nitriles of Arylglycines. HANS BUCHERER and ANDRÉ GROLEE (*Ber.*, 1906, **39**, 986—1013. Compare *Abstr.*, 1902, i, 533).—A number of nitriles of arylglycines have been prepared by (1) the condensation of aromatic amine hydrochlorides with aldehydes or ketones or their derivatives and solid potassium cyanide, suspended in benzene, ether, or light petroleum and (2) the condensation of ketonecyano-hydrins with amines in the same solvents. A table is given showing the substances used and the percentage yields of the products obtained.

The condensation products of aniline hydrochloride with ethyl acetoacetate and potassium cyanide and of *m*-xylydine hydrochloride with acetone and potassium cyanide are extremely unstable.

When fused with sodium ethoxide and potassium hydroxide at 270°, anilinoisobutyric acid, obtained by hydrolysis of the nitrile, prepared by the condensation of aniline with acetonecyanohydrin (Tiemann and Friedländer, *Abstr.*, 1882, 56), yields a substance, $C_{10}H_{11}ON$, which crystallises in small, white prisms, sublimes at 110° in glistening prisms, melts at 150—151°, and forms a dye when coupled with *p*-nitrophenyldiazonium chloride. If the acid is an α -anilino-compound, the product of fusion must be 2:2-dimethylindoxyl,



but 3-methyldihydro-4-carbostyryl, $C_6H_4 \begin{array}{c} \text{NH} \cdot CH_2 \\ \diagup \quad \diagdown \\ \text{CO} - CHMe \end{array}$, if derived from β -anilinoisobutyric acid (Bischoff and Mintz, *Abstr.*, 1892, 1338).

α -Anilino- α -phenylpropionitrile melts at 155—156° (m. p. 152°, Jacoby, *Abstr.*, 1886, 800).

α -*Toluidinoisobutyronitrile*, $C_{11}H_{14}N_2$, crystallises in very pale violet needles, melts at 78—79°, and decomposes readily. The *amide*, $C_{11}H_{16}ON_2$, melts at 131—132°.

α -*Toluidinophenylacetone*nitrile crystallises in rose-coloured leaflets and melts at 72—73° (m. p. 71°, Sachs, *Abstr.*, 1901, i, 272). The *amide*, $C_{15}H_{16}ON_2$, crystallises in small, white needles, melts at 125—126°, and on hydrolysis with concentrated hydrochloric acid yields the acid melting at 142—143°.

α -*p*-*Toluidinoisobutyronitrile*, $C_{11}H_{14}N_2$, crystallises in slender, glistening needles and melts at 73—74°. The *amide* crystallises in slender, white needles and melts at 141—143°.

α -*p*-*Toluidinophenylacetamide*, $C_{15}H_{16}ON_2$, crystallises in glistening leaflets and melts at 113—114°.

The condensation of *p*-toluidine hydrochloride and *p*-nitrobenzaldehyde in presence of potassium cyanide leads to the formation of *p*-nitrobenzylidene-*p*-toluidine, melting at 124—125°.

p-Aminophenol condenses with acetone and potassium cyanide, or with acetonecyanohydrin, to form a product, $C_{10}H_{12}ON_2$, which crystallises in small, glistening, almost white leaflets, melts at 137°, is soluble

in aqueous sodium hydroxide, and decomposes quickly on exposure to the air.

α-p-Hydroxyanilinophenylacetonitrile (Sachs and Goldmann, Abstr., 1902, i, 780) crystallises in slender, light yellow needles and melts at 113—114°. The *amide*, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CHPh} \cdot \text{CO} \cdot \text{NH}_2$, crystallises in small needles and melts at 142°.

The *nitrile*, $\text{C}_{11}\text{H}_{14}\text{ON}_2$, prepared from *p*-anisidine and acetonecyano-hydrin, melts at 47—48° and is very unstable.

α-p-Anisidinophenylacetonitrile melts at 73—74° (m. p. 85°, von Miller, Plöchl, and Scheitz, Abstr., 1899, i, 128).

The *nitrile*, prepared by the condensation of *p*-phenylenediamine hydrochloride, acetone, and potassium cyanide, crystallises in small needles, melts at 157—158°, and decomposes when dried in a desiccator.

The condensation of *p*-phenylenediamine hydrochloride, benzaldehyde, and potassium cyanide leads to the formation of *p*-phenylenediaminodiphenylacetonitrile, melting at 163° (Sachs and Goldmann, *loc. cit.*).

m-Tolylenediaminodisobutyronitrile, $\text{C}_6\text{H}_3\text{Me}(\text{NH} \cdot \text{CMe}_2 \cdot \text{CN})_2$, crystallises in small, glistening needles, melts at 85—86°, and when coupled with *p*-nitrophenyldiazonium chloride forms a yellow dye. The *amide* crystallises in small, white, nodular aggregates and melts at 200°.

Amino-m-tolylaminoisobutyronitrile, $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH} \cdot \text{CMe}_2 \cdot \text{CN}$, crystallises in white, unstable needles, melts at 90—91°, and becomes brown on exposure to air. The *amide* melts at 169°. When coupled with *p*-nitrophenyldiazonium chloride, the nitrile forms a reddish-yellow dye, $\text{C}_{17}\text{H}_{18}\text{O}_2\text{N}_6$, having a characteristic grey lustre, and when heated with concentrated sulphuric acid yielding a dark brown substance, $\text{C}(\text{NH}_2) \cdot \text{CH} \cdot \text{C} \cdot \text{N} \cdot \text{CH} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$
 $\text{CMe} = \text{CH} \cdot \text{C} \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$

Benzidinodisobutyronitrile, $\text{C}_{20}\text{H}_{22}\text{N}_4$, crystallises from a mixture of alcohol and ether. The *amide* forms small, glistening leaflets and melts above 255°.

The product of the condensation of phenylhydrazine with acetonecyano-hydrin is *α*-phenylhydrazinoisobutyronitrile, as it does not condense with carbon disulphide or with a second mol. of acetonecyano-hydrin (compare Reissert, Abstr., 1884, 1152; Eckstein, Abstr., 1893, i, 85).

The condensation of phenylhydrazine with ethyl acetoacetatecyano-hydrin leads to the formation of 1-phenyl-3-methylpyrazolone, melting at 127°.

The *nitrile*, $\text{C}_{14}\text{H}_{14}\text{N}_2$, prepared from *α*-naphthylamine hydrochloride and acetonecyano-hydrin, crystallises in colourless needles, which become bluish-violet on exposure to air, melts at 63—64°, and is readily decomposed by water or dilute hydrochloric acid. The *amide*, $\text{C}_{14}\text{H}_{16}\text{ON}_2$, crystallises in small, white needles and melts at 129—130°.

β-Naphthylaminoisobutyronitrile, $\text{C}_{14}\text{H}_{14}\text{N}_2$, is obtained as a crystalline powder, melts at 106—107°, is more stable than the *α*-compound, and on hydrolysis yields Bischoff and Mintz's *β*-naphthylaminoisobutyric acid, melting at 187—188° (*loc. cit.*). The *amide* crystallises in small,

glistening, white leaflets, becomes brown on exposure to air, melts at 168—169°, and dissolves in alcohol to form a fluorescent solution.

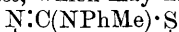
β -Naphthylaminophenylacetamide, $C_{18}H_{14}ON_2$, forms a white, crystalline powder and melts at 158—159°. The acid, $C_{18}H_{15}O_2N$, melts at 175—176°.

The condensation of phenol with benzaldehyde and potassium cyanide in benzene solution leads to the formation of *phenoxyphenylacetamide*, $OPh \cdot CHPh \cdot CO \cdot NH_2$, which melts at 139—140°, and when treated with concentrated sulphuric acid undergoes isomeric change, forming *hydroxydiphenylacetamide*, $OH \cdot C_6H_4 \cdot CHPh \cdot CO \cdot NH_2$, melting above 255°.

Resorcinol condenses with benzaldehyde and potassium cyanide, yielding a yellowish-brown, amorphous *product*, which contains carbon, hydrogen, and oxygen and melts above 255° or when heated with water.

G. Y.

New Oxidation Products of Unsymmetrical Disubstituted Aromatic Thiocarbamides. K. DOST (Ber., 1906, 39, 1014—1016. Compare Hofmann and Gabriel, Abstr., 1892, 1109).—The action of sulphur chloride on *as*-phenylmethylthiocarbamide in chloroform solution leads to the formation of a *hydrochloride*, $C_{16}H_{16}N_4S_2 \cdot 2HCl$, which crystallises in slender, white needles and melts above 275°. The *base*, which may have the constitution



or $NPhMe \cdot CS \cdot N:N \cdot CS \cdot NPhMe$, crystallises in large, white needles and melts at 128°. The *picrate*, $C_{16}H_{16}N_4S_2 \cdot 2C_6H_3O_7N_3$, crystallises in flocculent aggregates of needles and melts at 230°; the *nitrite*, $C_{16}H_{16}N_4S_2 \cdot 2HNO_2$, crystallises in matted, orange needles, commences to become red at 120°, and detonates at 153°.

The *base*, $C_{18}H_{20}N_4S_2$, obtained in the same manner from *as*-phenylethylthiocarbamide, crystallises in glassy, nodular aggregates and melts at 86°. The *hydrochloride*, melts at 253°; the *nitrite* forms red, hair-like needles and melts at 152°.

The *product*, $C_{26}H_{20}N_4S_2$, obtained from *as*-diphenylthiocarbimide, crystallises in shining, transparent prisms, melts at 150—210°, and does not form salts.

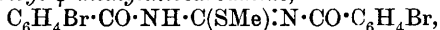
G. Y.

Molecular Rearrangement of Unsymmetrical Diacyl- ψ -thiocarbamides to Isomeric Symmetrical Derivatives. TREAT B. JOHNSON and GEORGE S. JAMIESON (Amer. Chem. J., 1906, 35, 297—309).—*as*-Dibenzoyl- ψ -methylthiocarbamide, $NBz_2 \cdot C(SMe) : NH$, obtained by adding benzoyl chloride to a solution of ψ -methylthiocarbamide in presence of potassium hydroxide, crystallises in needles, melts at 130—135° and evolves a small quantity of methyl mercaptan, then solidifies, and, on further heating, partially melts at 145—146° and decomposes at 175—185°. The compound is decomposed by sodium hydroxide solution into benzoic acid and benzoyl- ψ -methylthiocarbamide; it is also decomposed by boiling hydrochloric acid with formation of benzoic acid and an oily product containing sulphur. When this unsymmetrical ψ -thiocarbamide is heated for twenty minutes at 150°, it is converted into *s*-dibenzoyl- ψ -methylthiocarbamide,

$\text{NHBz}\cdot\text{C}(\text{SMe})\cdot\text{NBz}$, which crystallises in long, slender needles and melts at $147\text{--}148^\circ$; the same rearrangement takes place when an alcoholic solution of the unsymmetrical compound is submitted to prolonged boiling. When the symmetrical derivative is boiled with hydrochloric acid, it is converted into methyl mercaptan and *s*-dibenzoylcarbamide.

as-*Dibenzoyl-ψ-ethylthiocarbamide*, $\text{NBz}_2\cdot\text{C}(\text{SEt})\cdot\text{NH}$, melts partially at $104\text{--}105^\circ$, then solidifies completely, and afterwards melts at 110° . It is decomposed by sodium hydroxide or hydrochloric acid into benzoic acid and benzoyl-*ψ*-ethylthiocarbamide. When heated at its melting point, the compound undergoes rearrangement into *s*-dibenzoyl-*ψ*-methylthiocarbamide, $\text{NHBz}\cdot\text{C}(\text{SEt})\cdot\text{NBz}$, which crystallises in needles and melts at $110\text{--}111^\circ$. The symmetrical derivative is soluble in sodium hydroxide solution and is reprecipitated on neutralising with hydrochloric acid; it is decomposed by boiling hydrochloric acid into ethyl mercaptan and *s*-dibenzoylcarbamide.

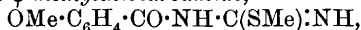
By the action of *p*-bromobenzoyl chloride on *ψ*-methylthiocarbamide, *s*-di-*p*-bromobenzoyl-*ψ*-methylthiocarbamide,



is obtained, which crystallises in needles and melts at 178° ; probably a small quantity of the unsymmetrical compound is also produced. When the symmetrical derivative is heated at its melting point, a small quantity of mercaptan is evolved, but otherwise the compound remains unaltered. It is decomposed by sodium hydroxide with formation of *p*-bromobenzoic acid; it is very stable towards hydrochloric acid, but when boiled with hydrobromic acid is converted into methyl mercaptan and *s*-di-*p*-bromobenzoylcarbamide, which melts and decomposes at $228\text{--}233^\circ$.

p-Bromobenzoylcarbamide, $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, obtained by the action of *p*-bromobenzoyl chloride on carbamide, forms microscopic crystals, melts and decomposes at $236\text{--}237^\circ$, and is slightly soluble in alcohol or water.

p-Methoxybenzoyl-*ψ*-methylthiocarbamide,



prepared by the action of anisyl chloride on *ψ*-methylthiocarbamide, crystallises in colourless, slender prisms, melts at $103\text{--}105^\circ$, and is very soluble in alcohol.

When *ψ*-methylthiocarbamide is treated with anisyl chloride (2 mols.), a product is obtained which is probably a mixture of as- and *s*-di-*p*-methoxybenzoyl-*ψ*-methylthiocarbamides. The symmetrical compound, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{C}(\text{SMe})\cdot\text{N}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, crystallises in needles, melts at $159\text{--}160^\circ$, and by the action of boiling hydrochloric acid is converted into methyl mercaptan and dianisylcarbamide, melting at $205\text{--}207^\circ$.
E. G.

Quinonoid *aci*-Nitrophenol Esters. ARTHUR HANTZSCH and H. GORKE (*Ber.*, 1906, 39, 1073—1084).—From the products of the reaction between anhydrous alkyl haloids and the carefully dried silver salts of nitrophenols below 18° , the authors have isolated, in addition to the ordinary ethers, which in the pure state are quite colourless, intensely-coloured *aci*-nitrophenol esters to the extent of

1—1.5 per cent., to which the structure $O:C_6H_4:NO\cdot OR$ is ascribed. The isomerides are separated by rapidly evaporating the solution in anhydrous ether in a vacuum over sulphuric acid; the indistinctly crystalline, red deposit on the sides of the vessel is separated from the less-intensely coloured well-defined crystals on the bottom of the beaker, dissolved in chloroform, and light petroleum is added drop by drop, causing a precipitation of the true ether. The ester, which remains in solution, has not been obtained pure, and still contains about 10 per cent. of nitrophenol ether.

Ethyl aci-trinitrophenol ester, $O:C_6H_2(NO_2)_2:NO\cdot OEt$, containing about 10 per cent. of the isomeric ether, is obtained from silver picrate and ethyl bromide. It forms an indistinctly crystalline red mass, melts at $50-52^\circ$, is unimolecular, dissolves readily in ether, alcohol, benzene, or chloroform, and is sparingly soluble in light petroleum. The dry solid changes within two months into the isomeric ether; the same change takes place more rapidly in anhydrous non-hydrolysing solvents, and almost instantaneously when hydrogen chloride, ammonia, or zinc dust is added to such solutions. Water and other hydrolysing solvents instantly destroy the red colour of the ester, this being due partly to the transformation into the ether, partly to hydrolysis and formation of picric acid.

Methyl aci-trinitrophenol ester, $O:C_6H_2(NO_2)_2:NO\cdot OMe$, melts between 40° and 42° .

Methyl aci-o-nitrophenol ester, $O:C_6H_4:NO\cdot OMe$, is a dark red liquid at the ordinary temperature, solidifying at -5° . It is decidedly more stable than the *aci*-trinitrophenol ester, can be preserved for a long time without loss of colour, and is comparatively slowly hydrolysed by water.

Ethyl aci-2:4-dinitrophenol ester, $O:C_6H_3(NO_2)_2:NO\cdot OEt$, is a very unstable red solid.

Similar compounds obtained from *p*-nitrophenol, 3:4-dinitro-naphthol, and possibly *m*-nitrophenol were detected by colour reactions but were not isolated and analysed. C. S.

Constitution and Colour of Nitrophenols. ARTHUR HANTZSCH (*Ber.*, 1906, 39, 1084—1105).—Mainly a discussion of the results mentioned in the previous abstract.

Nitrobenzene, obtained by nitrating pure benzene from benzoic acid, is rendered quite colourless by repeated fractionation, but becomes yellow again when kept. The three dinitrobenzenes, 1:2:4- and 1:3:5-trinitrobenzene, trinitrotoluene, trinitroxylene, and trinitrocumene are obtained colourless by repeated crystallisation; β -nitro-naphthalene separates from dilute alcoholic solution, after the use of animal charcoal, in colourless plates.

The author claims that all nitrophenol ethers, which are incapable of exhibiting tautomerism, are colourless, and, in accordance with this view, has prepared colourless specimens of trinitroanisole and trinitrophenetole by repeatedly shaking the dry ethereal solution of these ethers with sodium hydrogen carbonate until the colour has disappeared, rapidly evaporating the ether in a current of dry air, and allowing the residue to remain over phosphoric oxide; the colourless

crystals, which have the same melting point as the yellow form, are shown to be "optically" colourless in Koenig's spectrophotometer.

The ethereal solution of trinitrophenol acetate, obtained by the action of dry silver picrate on acetyl chloride dissolved in anhydrous ether, is "optically" colourless, and by evaporation over phosphoric oxide deposits colourless crystals, melting at 76° (compare Tommasi and David, this Journal, 1873, 1238) and rapidly turning yellow in the presence of water-vapour.

o-Nitroanisole, obtained from freshly-prepared, dried, and air-free materials, is rendered "optically" colourless by repeated distillation in a high vacuum; the melting point is 9.4°, 0.3° higher than that of the ordinary yellow ether. The corresponding acetate is also easily obtained in a colourless condition from absolute ethereal solution.

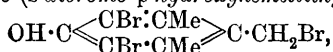
Nitrophenol derivatives, which are structurally incapable of exhibiting tautomerism, not only do not exercise selective absorption, but also remain "optically" colourless at varying temperatures and in different solvents, whereas the free nitrophenols under the same conditions exhibit a distinct change of colour. *p*-Nitrophenols and α -nitronaphthol show very little tendency to pass into the coloured *aci*-form; on the contrary, this tendency is so great with *o*-nitrophenols that they have not yet been obtained colourless.

m-Nitrophenol, 2:4-dinitrophenol, and picric acid have been obtained free from colour. Marcwald's "colourless" picric acid (Abstr., 1900, i, 391), when examined spectrophotometrically, is found to absorb violet rays; hence under all conditions picric acid contains the *aci*-form.

By a somewhat crude method, the amount of coloured *aci*-form existing in solid solution in the colourless nitrophenols is estimated at not more than about 1 per cent. even in the case of the intensely-coloured *o*-nitrophenol. An exact method of estimation is due to H. Gorke (*Diss.*, Leipzig, 1905).

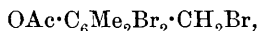
Assuming that in alkaline solution the nitrophenols are completely in the *aci*-form, the author shows that with increasing dilution the percentage of coloured ions in an aqueous solution of a nitrophenol, colorimetrically determined, increases *pari passu* with the degree of electrolytic dissociation. The more the coloured, dissociated *aci*-nitrophenols change into the undissociated molecules, so much the more real colourless nitrophenol is produced. C. S.

New Brominated ψ -Phenols. KARL AUWERS [and, in part, F. JESCHECK, OTTO SCHRÖTER, TH. MARKOVITS, and C. ROEVER] (*Annalen*, 1906, 344, 271—280).—3:5-Dibromo-4-hydroxy-2:6-dimethylbenzyl bromide (*s*-dibromo-*p*-hydroxyhemellithyl bromide),

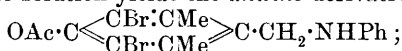


is prepared by the action of bromine on the corresponding phenolic alcohol in chloroform solution cooled by ice; it crystallises from glacial acetic acid in glistening leaflets, from benzene in slender needles, melts at 140—142°, and is readily soluble in most solvents with the exception of petroleum. As a ψ -phenol, it is insoluble in aqueous

alkali hydroxides, and shows the typical reactivity of the α -bromine atom. When reduced with zinc and much concentrated hydrochloric acid, it yields a small amount of impure *dibromohemellithenol*, $\text{OH}\cdot\text{C}\begin{smallmatrix} \text{CBr}\cdot\text{CMe} \\ \text{CBr}\cdot\text{CMe} \end{smallmatrix}\text{CMe}$, which melts at 172° . The *acetate*,

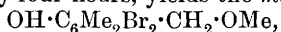


formed from the ψ -phenol, crystallises from alcohol or glacial acetic acid in glistening leaflets, melts at 151 – 158° , and when boiled with aniline in benzene solution yields the *aniline* derivative,



this crystallises in stout, glistening prisms, melts at 145 – 146° , is insoluble in aqueous alkali hydroxides, and is hydrolysed by digestion with an alcoholic alkali hydroxide, forming *dibromo-p-hydroxyhemellithylaniline*, $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{NHPh}$, which is formed also by the action of aniline on the ψ -phenol in benzene solution. It crystallises from dilute alcohol or light petroleum in slender, glistening needles and melts at $146\cdot5^\circ$.

Dibromo-p-hydroxyhemellithyl acetate, $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{OAc}$, formed by boiling the bromide with sodium acetate and glacial acetic acid, crystallises in short prisms, melts at 122 – 123° , is readily soluble in benzene, alcohol, or glacial acetic acid, and when boiled with methyl alcohol for one hour, or digested with methyl alcohol at the ordinary temperature for twenty-four hours, yields the *methyl ether*,



which crystallises in long, slender needles and melts at 103° . The action of aqueous acetone on the acetate leads to the formation of the *alcohol*, $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{OH}$, which crystallises in matted long, slender needles, melts at 179° , and is readily soluble in alcohol, acetone, ethyl acetate, or glacial acetic acid. The *diacetate*, $\text{C}_{13}\text{H}_{14}\text{O}_4\text{Br}_2$, crystallises in stellate aggregates of needles and melts at 122 – $124\cdot5^\circ$.

Dibromo-o-hydroxymesityl bromide, $\text{CBr}\begin{smallmatrix} \text{CMe}=\text{CBr} \\ \text{CMe}\cdot\text{C}(\text{OH}) \end{smallmatrix}\text{C}\cdot\text{CH}_2\text{Br}$, is obtained in a yield of 80–90 per cent. of the theoretical when *o*-hydroxymesityl alcohol cooled by ice, is treated with an excess of bromine; it crystallises in colourless needles, melts at 149 – 150° , and is insoluble in aqueous alkali hydroxides. The *monoacetate*,



separates from dilute methyl alcohol as a colourless powder, melts at 96 – 97° , and when finely divided is readily soluble in very dilute sodium hydroxide, but if treated with only moderately dilute sodium hydroxide is converted into the amorphous ψ -phenol, which is insoluble in aqueous alkali hydroxides. The *diacetyl* derivative, $\text{C}_{13}\text{H}_{14}\text{O}_4\text{Br}_2$, crystallises from light petroleum in long, slender needles or stout prisms and melts at 98 – 99° .

o-Hydroxyisoduryl bromide, $\text{OH}\cdot\text{C}\begin{smallmatrix} \text{CMe}=\text{CBr} \\ \text{C}(\text{CH}_2\text{Br})\cdot\text{CMe} \end{smallmatrix}\text{CMe}$, is prepared by the action of bromine on the phenolic alcohol in chloroform solution; it crystallises from a mixture of benzene and petroleum in stout, glistening prisms, is readily soluble in ether, chloroform, or glacial acetic acid, and is insoluble in aqueous alkali hydroxide, but on

treatment with alcohol is converted into the phenol, which is soluble in alkali hydroxides. G. Y.

Dinaphthylene Dioxide. ARCHIBALD A. NEIL (*Ber.*, 1906, **39**, 1059—1060).—*Dinaphthylene dioxide*, $C_{20}H_{12}O_2$, obtained as a by-product in the preparation of 2:3-dihydroxynaphthalene, crystallises from toluene in large, pearly leaflets and sublimes in colourless plates. Its solution in toluene has a slight violet fluorescence. The *compound*, $C_{20}H_{11}O_3$, also obtained as a by-product in the same preparation, forms colourless needles, dissolves in sodium hydroxide, and melts at 209—212° (compare Ullmann and Stein, this vol., 1, 258).

A. McK.

Onocerin (Onocol). FRANZ VON HEMMELMAYR (*Monatsh.*, 1906, **27**, 181—198. Compare Thoms, *Abstr.*, 1897, i, 201, 361).—When oxidised with chromic acid in glacial acetic acid solution at the ordinary temperature, onocol yields onoketone and *onoceric acid*, $C_{20}H_{30}O_4$. This melts to a resinous mass under boiling water; when dry, some preparations melted at 70—80°, others at 100—120°; it is readily soluble in alcohol, ether, benzene, or glacial acetic acid, becomes strongly electrified when rubbed, and is probably dibasic. The *silver* salt, $C_{20}H_{29}O_4Ag$, was analysed; the *barium* salt decomposes when washed with water. If the oxidation takes place in hot glacial acetic acid solution, *ψ-onoceric acid*, which contains a greater percentage of carbon than is required by the formula $C_{20}H_{30}O_4$, is formed; it resembles onoceric acid, and melts slowly after becoming soft at 80°. A diminution of the percentage of carbon in the acid product is observed if an excess of chromic acid is used either in cold or hot solution. The author could not obtain Thoms' acid, $C_{20}H_{40}O_2$ (*loc. cit.*).

When oxidised with nitric acid, onocol yields traces of acetic and butyric acids together with amorphous nitro-acids; if cold fuming nitric acid is used, the chief product is *dinitro-onoceric acid*, $C_{20}H_{28}O_4(NO_2)_2$, which is obtained as a yellow powder and melts and decomposes at about 180°. With hot concentrated nitric acid, yellow, amorphous *trinitro-onoceric acid*, $C_{20}H_{27}O_4(NO_2)_3$, melting and decomposing at 210—220°, is obtained.

Small amounts of acetic and butyric acids are formed also by the oxidation of onocol with chromic acid in concentrated sulphuric acid solution. Potassium permanganate has little action on onocol in neutral or alkaline solution, but in presence of an acid oxidises it completely to carbon dioxide and water. G. Y.

Hydrogenation of Cholesterol. CARL NEUBERG (*Ber.*, 1906, **39**, 1155—1158. Compare Diels and Abderhalden, this vol., i, 272).—On reducing cholesterol with sodium in boiling amyl alcohol, a *dihydro-cholesterol*, $C_{27}H_{46}O$, is obtained with a yield of 30—50 per cent.; it separates from alcohol in small, white, prismatic crystals, and after drying in a vacuum over phosphoric oxide melts at a temperature between 119° and 124°, depending on the rate of heating. It does not respond to the Salkowski or Obermüller tests, and differs from the parent cholesterol in being dextrorotatory, having $[\alpha]_D +18.35^\circ$ in

10 per cent. ethereal solution. Whether it is identical with natural coprosterol remains to be investigated.

W. A. D.

Reduction of α -isodypnopinacolin. F. V. DAELS (*Bull. Acad. roy. Belg.*, 1905, 585—601).—When α -isodypnopinacolin (Abstr., 1900, i, 603, 604) is reduced with sodium amalgam in alcohol, it furnishes, in addition to unidentified products, benzaldehyde, triphenylbenzene, and an *alcohol*, $C_{32}H_{28}O$, melting at 184° . When the reduction is effected by means of zinc dust and acetic acid, a better yield of the same alcohol is obtained, and it is accompanied by an *isomeride* which melts at 178° .

The alcohol, $C_{32}H_{28}O$, crystallises from alcohol or acetic acid in colourless needles, is not esterified by acetyl or benzoyl chloride, does not react with hydroxylamine or phenylhydrazine, and is not dehydrated when boiled for several days with acetic acid. A mixture of hydrochloric and acetic acids converts it into a *hydrocarbon*, $C_{32}H_{26}$, which crystallises in short, slender needles, melts at 180° , is not reduced by sodium amalgam in alcohol, and sublimes when heated under reduced pressure, for the most part unchanged. When distilled under reduced pressure, the alcohol is partially decomposed, yielding (1) a volatile liquid, probably identical with that produced by the distillation of dypnone (Abstr., 1900, i, 35), (2) a yellow resin having a strong odour of benzaldehyde, and (3) a semi-liquid brown resin containing some triphenylbenzene. When warmed with a dilute alcoholic solution of potassium hydroxide, it is converted into a third *isomeric alcohol*, which crystallises from acetic acid, benzene, or alcohol in colourless needles, melts at 162° , is without action, on phenylhydrazine or hydroxylamine, and when heated with a mixture of hydrochloric and acetic acids, or with acetyl chloride, is dehydrated, yielding the hydrocarbon $C_{32}H_{26}$ already noted. When distilled under reduced pressure, the same products are obtained as from the first isomeride.

The second alcohol, melting at 178° , obtained in the initial reaction, crystallises in lamellæ, is soluble in boiling acetic acid, and less so in boiling alcohol. When distilled under reduced pressure, it furnishes the same products as the two isomerides already described.

T. A. H.

Hofmann's Reaction. III. ERNST MOHR (*J. pr. Chem.*, 1906, [ii], 73, 228—238. Compare Abstr., 1905, i, 890; this vol., i, 252).—When prepared by Graebe and Rostovzeff's method (Abstr., 1902, i, 633), benzoylchloroamide is obtained as a sandy powder, which, after purification by solution in aqueous potassium hydroxide and precipitation with acetic acid, melts at 113 — 115° . It interacts with 1 mol. of potassium hydroxide according to the equation: $NHCl \cdot C(Ph) \cdot O + KOH = NPh \cdot CO + KCl + H_2O$, or with 2 mols. according to the equation: $NHCl \cdot C(Ph) \cdot O + 2KOH = NHPh \cdot CO_2K + KCl + H_2O$. If in the usual scheme representing the course of Hofmann's reaction: $NH_2 \cdot C(Ph) \cdot O \rightarrow NHCl \cdot C(Ph) \cdot O \rightarrow NCl \cdot C(Ph) \cdot OK \rightarrow NPh \cdot CCl \cdot OK(IV) \rightarrow$

$NPh \cdot C(OH) \cdot OK(V) \rightarrow NHPh \cdot CO_2K(VI) \rightarrow NH_3Ph$, substances V and VI are the tautomeric forms of the phenylcarbamate, substance IV is now the only hypothetical intermediate product.

G. Y.

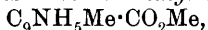
Formation of Amides and Hydrolysis of Esters by Amides.

HANS MEYER (*Monatsh.*, 1906, 27, 31—48).—The action of aqueous ammonia on an ester leads to the formation of the amide or to hydrolysis of the ester and formation of the ammonium salt; this, which is formed more often than is usually supposed (Hofmann, *Abstr.*, 1882, 950; Einhorn and Konek, *Abstr.*, 1893, i, 445), is the product of the interaction of ammonium hydroxide and the ester. The action of anhydrous gaseous or liquid ammonia on esters leads to the formation of a mixture of products (Tingle, *Abstr.*, 1900, i, 641; 1901, i, 200). The action of alcoholic ammonia on esters is reversible, and with an excess of alcohol the formation of the ester may be the chief reaction even at temperatures below 100° (Kirpal, *Abstr.*, 1901, i, 227). Digestion with concentrated aqueous ammonia in a closed vessel at the laboratory temperature or at 100° remains the best method of converting esters into amides.

When heated with saturated alcoholic ammonia at 125° for three hours, ethyl benzoate yields 16·8 per cent. (Fischer and Dilthey, *Abstr.*, 1902, i, 269), but on digestion with aqueous ammonia of sp. gr. 0·910 at the laboratory temperature for forty-eight hours, 60·8 per cent. of the theoretical amount of benzamide. Under the same conditions, 75 and 82 per cent., respectively, of the theoretical yield of phenylacetamide are obtained from ethyl phenylacetate.

The action of ammonia on an ester leads to the formation, in the first instance, of an additive compound, $R \cdot C(OH)(OEt) \cdot NH_3$, and the reaction must take place therefore the more readily the stronger the acid, that is, the more negative the group R. Thus ethyl trichloroacetate interacts readily with ammonia to form the amide, whereas trimethylacetamide is not obtained from the ester. The formation of the amide may be hindered also by the presence of other substituting groups.

3-Methylcinchonyl chloride, formed by boiling 3-methylcinchonic acid with thionyl chloride, crystallises in nodular aggregates of almost colourless needles and melts at 175°. *Methyl 3-methylcinchonate*,



formed by the action of methyl alcohol on the acid chloride, or of diazomethane on the acid, crystallises in colourless needles, melts at 77°, remains unchanged when digested with alcoholic ammonia at the laboratory temperature, and is hydrolysed completely by aqueous ammonia at 130°.

3-Methylcinchonamide, $C_9NH_5Me \cdot CO \cdot NH_2$, is formed from the acid chloride; it separates from alcohol in dull, colourless crystals, melts at 229—230°, is hydrolysed only slowly by boiling 10 per cent. aqueous potassium hydroxide, and remains unchanged when heated with aqueous ammonia at 130° for three hours.

Ethyl 2-hydroxy-1-naphthoate remains unchanged when digested with aqueous ammonia at the laboratory temperature for some weeks, but is decomposed when heated at 100° for some hours, forming chiefly β -naphthol and ammonium carbamate. The amide, formed by the thionyl chloride method (*Abstr.*, 1902, i, 31), remains unchanged when heated with aqueous ammonia at 100°. The methyl esters of the fatty acids interact with ammonia to form the corresponding amides, more

easily than do the ethyl esters (compare Hofmann, *loc. cit.* ; van Linge Abstr., 1897, i, 618).

The corresponding amides were obtained from the following methyl esters, in yields of the percentages of the theoretical given: methyl *n*-butyrate, 84 per cent.; methyl *isobutyrate*, 91 per cent.; methyl valerate, 78 per cent.; methyl hexoate, 45 per cent.; methyl arachate, about 15 per cent. Under the same conditions, hexoamide was obtained from the ethyl ester in a yield of only 3 per cent. of the theoretical.

Methylmalonamide is obtained in a yield of 93 per cent., dimethylmalonamide in a yield of 81 per cent., when the corresponding dimethyl esters are digested with aqueous ammonia at the laboratory temperature for twelve and twenty-four hours respectively. Dimethyl diethylmalonate remains unchanged when digested with aqueous ammonia (compare this vol., i, 137). G. Y.

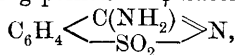
Linking of Amino-acids. ERNST MOHR and FRIEDRICH KÖHLER (*Ber.*, 1906, 39, 1057—1058).—*o*-Aminobenzoylanthranilic acid, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, prepared from its sodium salt, obtained by the interaction of phthalimide, sodium hydroxide, and sodium hypochlorite in aqueous solution, crystallises in needles and melts at 202—203°. Its acetyl derivative melts at 223—224° (compare Anschütz, Schmidt, and Greiffenberg, Abstr., 1903, i, 57).

A. McK.

***o*-Sulphaminebenzoic Acid and Related Compounds.** HAMILTON BRADSHAW (*Amer. Chem. J.*, 1906, 35, 335—340).—Wilson (Abstr., 1904, i, 51) has found that *o*-sulphaminebenzoic acid crystallises either in plates or needles. A study has been made of the conditions under which each of these forms is produced.

The compound, melting at 263°, which was obtained by Wilson (*loc. cit.*) by the action of ammonium thiocyanate on *o*-sulphaminebenzoic acid is not the diamide, but is ammonium *o*-carbaminebenzenesulphonate.

By the action of phosphorus oxychloride on potassium *o*-carbaminebenzenesulphonate, Wilson (*loc. cit.*) obtained a compound which he regarded as *o*-carbaminebenzenesulphonic chloride. By treating the same potassium salt with phosphorus pentachloride, Sohon (Abstr., 1898, i, 429) obtained *o*-cyanobenzenesulphonic chloride, a compound which was also obtained by Jesurun (Abstr., 1893, i, 715) by heating benzoic sulphinide with phosphorus pentachloride. It has now been found that the same chloride, melting at 69—70°, is obtained by each of the three methods. Jesurun's results on the action of ammonia on *o*-cyanobenzenesulphonic chloride (*loc. cit.*) have been confirmed except with regard to the melting points. "*ψ*-Saccharinamide,"



melts at 297° (uncorr.). *o*-Cyanobenzenesulphonamide melts at 160° (uncorr.) and is simultaneously converted into "*ψ*-saccharinamide."

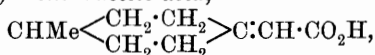
When *o*-cyanobenzenesulphonamide is heated with dilute sodium hydroxide, it is converted into benzoicsulphinide.

By the action of sodium hypobromite on potassium *o*-carbamine-benzenesulphonate, aniline-*o*-sulphonic acid is produced. E. G.

Optically-active Substances which do not contain an Asymmetric Atom. WILLY MARCKWALD and RICHARD METH (*Ber.*, 1906, 39, 1171—1177. Compare Perkin and Pope, *Proc.*, 1906, 22, 107).—1-Methylcyclohexane-4-one combines with ethyl iodoacetate or ethyl bromoacetate in presence of magnesium, giving *ethyl 1-methylcyclohexane-4-ol-4-acetate*,

$$\text{CHMe} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et},$$

which on hydrolysis gives rise to two *acids*, which are probably *cis* and *trans* isomerides; α -1-methylcyclohexane-4-ol-4-acetic acid is sparingly soluble in water and melts at 140—141°, the isomeric β -acid being much more soluble in water and melting at 78—81°. Both acids when heated with 30 per cent. sulphuric acid give rise to the same 1-methylcyclohexylidene-4-acetic acid,



which, when purified by means of the *barium* salt, melts at 40.5—41°; this acid is sparingly soluble in water, reduces potassium permanganate, when heated with aqueous potassium hydroxide gives 4-methylhexanone, and with cinchonine yields a *salt*, $\text{C}_{19}\text{H}_{21}\text{ON}_2 \cdot 2\text{C}_9\text{H}_{14}\text{O}_2$, which is sparingly soluble in light petroleum and melts at 56—63°. This salt on being decomposed with dilute sulphuric acid gives *d*-1-methylcyclohexylidene-4-acetic acid, which has $[\alpha]_D + 9.3^\circ$. The light petroleum mother liquors of the cinchonine salt give the 1-1-methylcyclohexylidene-4-acetic acid with $[\alpha]_D - 10.4^\circ$.

The authors have repeated the work of Erlenmeyer, jun. (*Abstr.*, 1905, i, 892; this vol., i, 21, 176) with cinnamic acid and have failed to confirm his results; on preparing in alcoholic solution the brucine salt of cinnamic acid from storax, the salt melting at 107—113° could alone be obtained, with a specific rotatory power $[\alpha]_D - 16.5^\circ$ to -19.5° . The same salt was obtained from synthetical cinnamic acid. W. A. D.

NOTE.—Perkin and Pope (*loc. cit.*) have prepared 1-methylcyclohexylidene-4-acetic acid by another method; their product is not identical with the acid described above. W. A. D.

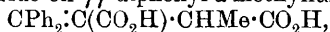
Relative Rates of Oxidation of ortho-, meta-, and para-Compounds. HAMILTON BRADSHAW (*Amer. Chem. J.*, 1906, 35, 326—335).—Determinations have been made of the relative rates of oxidation of the following substances by potassium permanganate at the ordinary temperature: *o*-, *m*-, and *p*-hydroxybenzoic acids; *o*-, *m*-, and *p*-aminobenzoic acids; *o*-, *m*-, and *p*-nitrophenols; *o*-, *m*-, and *p*-nitroanilines, and *o*-, *m*-, and *p*-toluidines. The results are tabulated.

When the hydroxybenzoic acids are treated with a neutral solution of potassium permanganate, the ortho-compound is the most readily oxidised and the para-compound the least. The influence of alkali hydroxide and of sulphuric acid on the rate of oxidation of these acids was studied, and it was found that the effect of the alkali hydroxide depends only on its concentration and not on the actual quantity present. Since, during the oxidation of organic substances, potassium

hydroxide is formed by the reduction of the permanganate, and becomes neutralised to a greater or less extent by the acid products of the oxidation, it was considered more satisfactory to use solutions containing a considerable amount of potassium hydroxide. Under these conditions, the order of the velocity of oxidation was, in all cases, meta, ortho, para, the meta-compounds being oxidised the most rapidly and the para-compounds the least. E. G.

Preparation of Salicylic Acid from *o*-Cresol, and a New Method of preparing Aurin. CHRISTIAN RUDOLPH (*Zeit. angew. Chem.*, 1906, 19, 384—385).—When a solution of *o*-cresol in concentrated sodium hydroxide is heated under pressure at 170—190° in the presence of sodium chromate, a deep red solution is obtained resembling an alkaline solution of rosolic acid; the reaction is probably due to the oxidation of some of the *o*-cresol to salicylic aldehyde, which then condenses with two more mols. of *o*-cresol to form a trihydroxytriphenylmethane. Aurin was prepared by heating a solution of 108 grams of *p*-cresol and 188 grams of phenol in 400 grams of 32 per cent. sodium hydroxide with a solution of 300 grams of sodium dichromate in 250 grams of 32 per cent. sodium hydroxide for some hours under pressure at 180°. The aurin was extracted from the mixture by means of sodium hydrogen sulphite. P. H.

Indoneacetic Acids. III. "Indonisation" and "Anhydri- sation." HANS STOBBE and FERDINAND GOLLÜCKE (*Ber.*, 1906, 39, 1066—1069. Compare Abstr., 1902, i, 542; 1904, i, 503).—The action of acetyl chloride on $\gamma\gamma$ -diphenyl- α -methylitaconic acid,

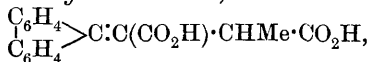


is analogous with that on diphenylitaconic acid itself, $\gamma\gamma$ -diphenyl- α -methylitaconic anhydride, $\text{C}_{18}\text{H}_{14}\text{O}_3$, being formed; it separates from carbon disulphide in prisms and melts at 146°.

γ -Phenyl- α -indonepropionic acid, $\text{C}_6\text{H}_4\langle\text{CPh}\rangle\text{C}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, prepared by the action of sulphuric acid on $\gamma\gamma$ -diphenyl- α -methylitaconic acid, has an orange colour and melts at 168°. Its solution in concentrated sulphuric acid is dark green.

The lactone of 3-hydroxy-3-phenyl-1-hydrindone-2-propionic acid, $\text{C}_6\text{H}_4\cdot\text{CPh}\text{---}\text{O}\rangle\text{CO}$, obtained as a by-product of the action of sulphuric acid on $\gamma\gamma$ -diphenyl- α -methylitaconic acid, separates from ether in colourless plates and from chloroform in prisms; it melts at 94°. Its solution in sodium hydroxide is first yellow and then becomes orange.

$\gamma\gamma$ -Diphenylene- α -methylitaconic acid,



prepared by the condensation of fluorenone with ethyl pyrotartrate in the presence of sodium ethoxide, separates from chloroform in yellow crystals and melts and decomposes at 158°. The anhydride, prepared

from it by the action of acetyl chloride, is yellow and melts at 147—148°. It does not form an indone compound when treated with sulphuric acid.

A. McK.

$\gamma\gamma$ -Diphenyl- α -methylitaconic Acid. HANS STOBBE and MAX NOETZEL (*Ber.*, 1906, 39, 1070—1072. Compare preceding abstract).— $\gamma\gamma$ -Diphenyl- α -methylitaconic acid (Abstr., 1896, i, 234) in chloroform solution does not react with bromine in diffused daylight; the addition takes place readily when cold water is added, a dibromide being produced which loses hydrogen bromide spontaneously to form

β -bromo- $\gamma\gamma$ -diphenyl- α -methylparaconic acid, $\text{CO}_2\text{H}\cdot\text{CBr}\begin{matrix} \text{CPh}_2-\text{O} \\ | \\ \text{CHMe}\cdot\text{CO} \end{matrix}$.

The latter melts and decomposes at 174.5° and, when heated or boiled with water, loses hydrogen bromide to form the stable $\gamma\gamma$ -diphenyl- α -methylitaconic acid, $\text{CO}_2\text{H}\cdot\text{C}\begin{matrix} \text{CPh}_2-\text{O} \\ \diagup \quad \diagdown \\ \text{CMe}-\text{CO} \end{matrix}$, which separates from water in

prisms and melts at 180—181°. The calcium and silver salts are described.

A. McK.

Additive Processes. DANIEL VÖRLANDER (*Annalen*, 1906, 345, 155—250. Compare Abstr., 1903, i, 495, 632; 1904, i, 65; 1905, i, 792).—Recent observations by various investigators, which throw light on the existence of two types of compounds, the unstable A type and the relatively more stable B type (*loc. cit.*), are discussed. The two series of salts of trialkyltrimethylenetriamine (Einhorn and Prettner, Abstr., 1904, i, 978) appear to illustrate this phenomenon remarkably clearly. The linking of carbon with carbon belongs in general to the B type, but Gomberg's triphenylmethyl appears to yield a hexaphenylethane of the A type.

[With FRANZ KÖTHNER.]—*Pulegone and Alkyl Sodiomalonates.*—Pulegone and ethyl sodiomalonate react in benzene solution, yielding the anhydride of the monoethyl ester of pulegonemalonic acid,

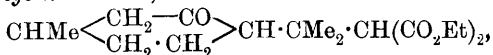
$\text{CHMe}\cdot\text{CH}_2\cdot\text{C}\begin{matrix} \text{O} \\ | \\ \text{CO} \end{matrix}$
 $\text{CH}_2\text{—CH}_2\text{—C}\begin{matrix} \text{O} \\ | \\ \text{CO} \end{matrix}\cdot\text{CMe}_2\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, which can be isolated by a careful series of fractional distillations as an oil boiling at 193—195° under 20 mm. and at 201—205° under 24 mm. pressure; it decolorises bromine slowly, hydrogen bromide being evolved and a brown, unstable oil produced. When hydrolysed, it yields the ketodilactone (pulegone-

$\text{CHMe}\cdot\text{CH}_2\cdot\text{C}\begin{matrix} \text{O} \\ | \\ \text{CO} \end{matrix}$
malonicdilactone), $\begin{matrix} | & & | \\ | & & | \\ | & & | \\ | & & | \\ | & & | \\ | & & | \end{matrix}$, melting at 104°

(Abstr., 1899, i, 259). With ammonia it yields the anhydride of pulegoneacetamide (m. p. 141—143°). Methyl sodiomalonate yields the corresponding methyl ester of the anhydride of pulegonemalonic acid, $\text{C}_{14}\text{H}_{20}\text{O}_4$; it is isolated by fractional distillation under reduced pressure and crystallises from petroleum in needles melting at 75—76°, and has $[\alpha]_D$ in methyl-alcoholic solution = +26.0—26.6° at 20°.

Hydrolysis of either of the esters of the anhydride affords a very good method of preparing the ketodilactone, details of which are given; this substance has $[\alpha]_D + 13.0^\circ$ at 33° in alcoholic solution, and 13.73° at 20° in chloroform solution. Menthone, $C_{10}H_{18}O$, boiling at $98-99^\circ$ under 19 mm. pressure, is also a by-product of the reaction.

Ethyl pulegonemalonate,



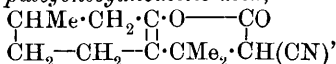
prepared by heating an alcoholic solution of the pulegonemalonedi-lactone with sulphuric acid, is purified by careful fractionation of the crude product, and is an oil boiling at $209-210^\circ$ under 25 mm. pressure, and has $[\alpha]_D - 3.27^\circ$ at 20° in alcoholic solution. In the reaction, pulegone and ethyl malonate are formed; ethyl pulegone-acetate is also produced, carbon dioxide being at the same time evolved. *Methyl pulegonemalonate* is obtained in a similar manner, and forms crystals melting at 51° and boiling at $187-188^\circ$ under 15 mm. pressure, and has $[\alpha]_D - 8.74-8.79^\circ$ at 20° in methyl-alcoholic solution.

Both esters are partially decomposed by sodium methoxide or ethoxide respectively into pulegone and the alkyl malonate, an equilibrium: pulegone + alkyl sodiomalonate + alcohol \rightleftharpoons alkyl pulegonemalonate + sodium ethoxide, being established. The medium greatly affects the point of equilibrium, in benzene the additive product being mainly formed, in alcohol pulegone and malonic ester. Very little addition takes place at a higher temperature.

With ammonia, the esters give a mixture of the anhydride of pulegoneacetamide and the monoamide of pulegonemalonic acid. The latter melts at 125° , at the same time losing water and carbon dioxide, becoming converted into the amide-anhydride.

On distilling the barium salt of pulegonemalonic acid, prepared from the ketodilactone and barium hydroxide, pulegone is alone formed.

The *anhydride of pulegonecyanoacetic acid*,



prepared from pulegone, ethyl cyanoacetate, and sodium in the presence of benzene, and then hydrolysing the product with potassium hydroxide, is purified by fractional distillation under reduced pressure, and crystallises in prisms melting at $75-76^\circ$; it reduces permanganate and decolorises bromine immediately. It is converted by alcoholic ammonia into the *amideanhydride* of pulegonecyanoacetic acid, which forms rhombic crystals, subliming without melting above 300° , a sublimate of prismatic needles being formed. If the product of the interaction of pulegone and ethyl cyanoacetate is heated with alkali hydroxide and then acidified, pulegonemalonedi-lactone is formed.

When pulegone is boiled with an alcoholic solution of sodium ethoxide, a substance, $C_{20}H_{30}O$ (?), is formed, which can be isolated by fractional distillation under reduced pressure; it is a pale yellow oil with a green fluorescence, boiling at $200-204^\circ$ under 20 mm. pressure and having $[\alpha]_D + 30.23-30.92^\circ$ at 20° in alcoholic solution. It is probably a condensation product.

[With ALFRED MAY and WILHELM KÖNIG.]—*Pulegoneacetic Acid*.—

The *anhydride* of pulegoneacetic acid, $\begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \cdot \text{C} \cdot \text{O} \text{---} \text{CO} \\ | \\ \text{CH}_2 \text{---} \text{CH}_2 \cdot \text{C} \cdot \text{CMe}_2 \cdot \text{CH}_2 \end{array}$, is prepared from pulegonemalonidilactone, which is heated until the evolution of carbon dioxide ceases, and then distilled under reduced pressure, when it boils at 178° under 30 mm. pressure; it crystallises in prismatic needles melting at 44° , has $[\alpha]_D + 71.13$ — 71.61° at 20° in alcoholic solution, and decolorises bromine and permanganate immediately, in the latter case hydrobromic acid being evolved.

Pulegoneacetic acid, $\begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO} \\ | \\ \text{CH}_2 \text{---} \text{CH}_2 \cdot \text{CH} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \end{array}$, is prepared by treating the anhydride with alcoholic potassium hydroxide and subsequently liberating the acid from the potassium salt; it forms colourless crystals melting at 67 — 68° and has $[\alpha]_D - 2.6$ — 3.2° at 20° in alcoholic solution. When heated at 130° , the anhydride is formed, the same reaction being brought about more easily in the presence of acetic anhydride. The *anhydride* of pulegoneacetamide, $\begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \cdot \text{C} \cdot \text{NH} \text{---} \text{CO} \\ | \\ \text{CH}_2 \text{---} \text{CH}_2 \cdot \text{C} \cdot \text{CMe}_2 \cdot \text{CH}_2 \end{array}$, is formed when the anhydride of pulegoneacetic acid is treated with ammonia, or when the pulegonemalonidilactone is heated with alcoholic ammonia under pressure; it crystallises in needles melting at 140 — 141° and has $[\alpha]_D + 65.88$ — 65.99° at 20° in alcoholic solution. The anhydride yields crystalline derivatives with ethylamine and phenylhydrazine.

The *semicarbazone* of pulegoneacetic acid, prepared from the acid and semicarbazide, forms white crystals melting and decomposing at 186 — 188° . *Methyl pulegoneacetate*, prepared from the anhydride and methyl alcohol in the presence of sulphuric acid, is an oil boiling at 155 — 157° under 24 mm. pressure and having $[\alpha]_D - 6.58$ — 6.88° at 20° in methyl-alcoholic solution. The *ethyl* ester boils at 166.5 — 169° under 25 mm. pressure and has $[\alpha]_D - 0.8$ — 1.13° at 20° in alcoholic solution. Both esters are converted into the anhydride of pulegoneacetamide by treatment with ammonia.

When pulegonemalonidilactone is reduced with sodium and alcohol, an *anhydride* of *pulegolacetic acid*, $\begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{O} \text{---} \text{CO} \\ | \\ \text{CH}_2 \text{---} \text{CH}_2 \cdot \text{CH} \cdot \text{CMe}_2 \cdot \text{CH}_2 \end{array}$, is formed; it is purified by fractional distillation, and boils at 175 — 180° under 16 mm. pressure; at low temperatures, it solidifies in crystals which melt at 33° and has $[\alpha]_D + 18.21^\circ$ at 20° in alcoholic solution. With barium hydroxide, the anhydride is converted into *barium pulegolacetate*, $(\text{C}_{12}\text{H}_{21}\text{O}_3)_2\text{Ba}$.

On reducing the anhydride of pulegoneacetic acid with sodium and alcohol, a second *anhydride* of pulegolacetic acid, stereoisomeric with that just described, is formed; it forms colourless crystals melting at 54° , and boils at 167° under 22 mm. pressure, and has $[\alpha]_D + 21.65^\circ$ at 20° in alcoholic solution; at the same time, menthone is formed, which distils over in the first fraction. Further, in the residue left after the distillation of the anhydride, a substance is contained which distils at 168 — 170° under 22 mm. pressure and has $[\alpha]_D + 16.5^\circ$ at 20° in alcoholic solution.

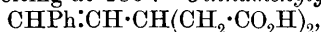
Pulegonemalonidilactone and pulegone- and pulegol-acetic anhydrides

yield with excess of alkali hydroxides the corresponding salts of the acetates; solutions of these salts are slowly converted into the anhydrides and alkali hydroxide.

[With PAUL GROEBEL.]—*Addition of Malonic Ester to Cinnamylideneacetone and Ethyl Cinnamenylacrylate.*—Cinnamylideneacetone and ethyl sodiomalonate combine to form hydroresorcinol derivatives, the constitutions of which depend on whether the ethyl malonate becomes attached to the $\alpha\beta$ -, the $\alpha\delta$ -, or the $\gamma\delta$ -positions in the group $C:C:C:C:O$; the constitution can be determined by oxidising these derivatives first with bleaching powder and then oxidising the unsaturated dicarboxylic acid with permanganate, when certain acids will be produced which will determine the constitution of the original material. Since tricarballic and benzoic acids are produced, it follows that the original additive product was a cinnamenyldihydroresorcin, $CHPh:CH\cdot CH<\begin{smallmatrix} CH_2\cdot CO \\ CH_2\cdot CO \end{smallmatrix}>CH_2$, the addition having taken place in the $\alpha\beta$ -position.

A similar addition takes place in the case of ethyl cinnamenylacrylate.

Cinnamenyldihydroresorcin was prepared by reducing cinnamylideneacetone with ethyl malonate in absolute alcoholic solution in the presence of sodium ethoxide; the sodium salt of ethyl cinnamenyldihydroresorcyate, which is first formed, is hydrolysed with sodium carbonate and the free acid obtained on acidifying boiled until the evolution of carbon dioxide ceases; the compound crystallises in colourless needles melting at 186° . *Cinnamenylglutaric acid*,



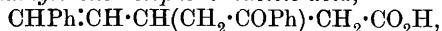
is obtained by oxidising an alkaline solution of the compound just mentioned with bleaching powder; it crystallises in lustrous leaflets melting at 134 — 135° . The *dimethyl* ester prepared from the acid and methyl alcohol in the presence of sulphuric acid crystallises in slender needles melting at 69 — 70° . *Cinnamenylglutaric anhydride*, prepared by heating the acid for several hours with acetic anhydride, which is subsequently distilled, crystallises in needles sintering at 135° and melting at 138° . If the anhydride is treated with aniline in a benzene solution, the *anilido-acid*, $CHPh:CH\cdot CH(CH_2\cdot CO\cdot NHPh)\cdot CH_2\cdot CO_2H$, is obtained as needles sintering at 139° and melting at 142° .

The cinnamenylglutaric acid was oxidised by alkaline permanganate solution, which was immediately decolorised, the odour of benzaldehyde becoming apparent. The excess of permanganate is removed by hydrogen peroxide, the liquid neutralised by acetic acid, and lead acetate added to precipitate the lead tricarballic acid; benzoic acid is obtained from the mother liquor. The tricarballic acid was completely identified by conversion into the anhydro-acid and into the anilido-acid, which it forms with *o*-toluidine.

Ethyl cinnamenylacrylate reacts with ethyl malonate in the presence of sodium ethoxide in alcoholic solution, giving a compound which, heated at 160° , yields β -cinnamenylglutaric acid (m. p. 134°). Methyl cinnamenylacrylate, prepared from the acid and methyl alcohol in the presence of acetic acid, crystallises in leaflets melting at 71° .

[With HERMANN STAUDINGER.]—*Cinnamylideneacetophenone and*

Ethyl Sodiomalonate.—Cinnamylideneacetophenone readily reacts with ethyl sodiomalonate in ethereal solution, forming *ethyl cinnamylideneacetophenonemalonate*, $\text{CHPh}:\text{CH}:\text{CH}(\text{CH}_2\cdot\text{COPh})\cdot\text{CH}(\text{CO}_2\text{Et})_2$, which crystallises in needles melting at $92-93^\circ$. The corresponding *acid* is readily obtained from the ester by hydrolysis, and crystallises in needles melting at 163° , carbon dioxide being at the same time evolved. *Cinnamylideneacetophenoneacetic acid*,



prepared by heating the corresponding acid at $165-170^\circ$, crystallises in needles melting at 125° . The *ethyl* ester crystallises in needles melting at $75-76^\circ$. When oxidised by an alkaline solution of permanganate, the acid last mentioned yields a mixture of benzoic and phenacysuccinic acids.

Cinnamylideneacetophenone and ethyl acetoacetate condense in ethereal solution, forming the compound $\text{C}_{23}\text{H}_{22}\text{O}_3$, which crystallises in needles melting and decomposing at $142-143^\circ$. When the ester is hydrolysed, a compound $\text{C}_{20}\text{H}_{18}\text{O}$, which is also produced in the original condensation, is obtained; it crystallises in needles melting at 106° .

[With PAUL WEISSHEIMER and FRITZ SPONNAGEL.]—*Ethyl Sorbate and Ethyl Sodiomalonate*.—In the formation of the condensation-product of ethyl sorbate and ethyl sodiomalonate, the addition takes place at the $\alpha\delta$ -position, the additive product having probably the constitution $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CHMe}\cdot\text{CH}(\text{CO}_2\text{Et})_2$; the condensation is brought about in benzene solution in the presence of sodium hydroxide, but on attempting to isolate the acid formed by hydrolysis of the primary product, carbon dioxide is evolved and *methylheptenedicarboxylic acid* formed. The latter could not be purified, but was converted into the *ethyl* ester, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, which boils at $158-160^\circ$ under 26 mm. pressure; it decolorises a bromine solution and reduces permanganate. When the crude methylheptenedicarboxylic acid was oxidised with permanganate, pyruvic and oxalic acids were alone obtained, although both tricarballic acid and β -methylglutaric acid were sought for.

All attempts to reduce the dicarboxylic acid to methylpimelic acid, or to condense the diethyl ester with ethyl sodiomalonate, failed.

[With ERNST STRUNCK.]—*Action of Alkyl Sodiomalonates on $\beta\gamma$ -Unsaturated Alkyl Carboxylates*.—A very large number of $\beta\gamma$ - and $\gamma\delta$ -unsaturated acids and other unsaturated compounds which do not contain a carbonyl group have been tested with respect to their reactivity with ethyl sodiomalonate. It was found that the $\gamma\delta$ -unsaturated compounds did not react, whilst of the $\beta\gamma$ -substances investigated only ethyl phenylisocrotonate reacted at all readily.

Ethyl phenylisocrotonate, $\text{CHPh}:\text{CH}:\text{CH}_2\cdot\text{CO}_2\text{Et}$, can be prepared from the acid and purified by fractionation; it is an oil boiling at 183° under 30 mm. pressure; it changes on keeping, and gives gradually a coloration with ferric chloride. The ester prepared from the silver salt, on the other hand, can be kept unchanged and gives no coloration with ferric chloride. The *methyl phenylisocrotonate* boils at 180.5° under 20 mm. pressure.

The ester was condensed with ethyl sodiomalonate in benzene solu-

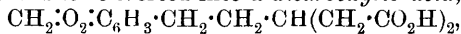
tion and the product hydrolysed with potassium hydroxide, a *tricarboxylic acid*, $C_{13}H_{14}O_6$, being formed; it is difficult to obtain in a pure state, and melts with evolution of carbon dioxide at 146° .

β -Benzylglutaric acid, $CH_2Ph \cdot CH(CH_2 \cdot CO_2H)_2$, is prepared by heating small quantities of the tricarboxylic acid at 160° and recrystallising the product from water, from which it separates in leaflets melting at 102° . The *diethyl ester* is an oil boiling at 188 — 189° under 17 mm. pressure; it decolorises permanganate and gives an intense green coloration with ferric chloride, reactions, however, which were traced to a minute trace of impurity present probably in the ethyl phenylisocrotonate. The *anhydride* of *β -benzylglutaric acid* is obtained by heating the acid with acetyl chloride; it melts at 85° and gives no reaction with ferric chloride or permanganate. With α -naphthylamine, it yields an *α -naphthylamido-acid*, which crystallises in needles melting at 154° .

Dilute nitric acid does not attack *β -benzylglutaric acid*, but the concentrated acid at 60° converts it into a *nitro-compound*, $C_{12}H_{13}O_6N$, which crystallises in needles melting at 163° .

Phenylacetaldehyde condenses with malonic acid in the presence of pyridine, forming a mixture of the $\alpha\beta$ - and the $\beta\gamma$ -phenylcrotonic acids. If the condensation is carried out in acetic acid, then the $\beta\gamma$ -acid is alone formed. Ethyl malonate and phenylacetaldehyde condense in the presence of diethylamine, forming a mixture of substances which, after hydrolysis, lose carbon dioxide and leave a mixture of *β -benzylglutaric acid* and *phenyl- $\beta\gamma$ -crotonic acid*.

Ethyl *$\beta\gamma$ -hydropiperate*, $C_{14}H_{16}O_4$, prepared from the silver salt, boils at 230° under 45 mm. pressure; it condenses with ethyl sodiomalonate in benzene solution, but only a small quantity of a condensation product could be isolated; it appeared to be identical with the dicarboxylic acid (m. p. 123°) which is formed from ethyl $\alpha\beta$ -hydropiperate and ethyl sodiomalonate. Ethyl *$\alpha\beta$ -hydropiperate*, prepared from the silver salt, is an oil boiling at 235 — 240° under 30 mm. pressure; it condenses with ethyl sodiomalonate, yielding a tricarboxylic acid, $C_{15}H_{16}O_8$, which crystallises in needles; at 80° it begins to lose carbon dioxide and is converted into a *dicarboxylic acid*,



which crystallises in leaflets melting at 125° . K. J. P. O.

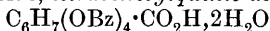
Quinic Acid. P. ECHTERMEIER (*Arch. Pharm.*, 1906, **244**, 37—57).—*Cinchonine*, *quinidine*, *cinchonidine*, *quinine*, and *strychnine* *quinates* are crystalline and contain each one molecule of the base and one molecule of the acid with 10, 2, 4, 3, and $1H_2O$ respectively; the first four melt, decomposing sometimes as they melt, at 195 — 196° , 178 — 179° , 216° , and 187 — 188° respectively; only the cinchonidine salt crystallises readily.

Methyl quinate, $C_6H_7(OH)_4 \cdot CO_2Me$, was prepared by boiling a mixture of methyl iodide and methyl alcohol with silver quinate; it melts at 126° to a milky liquid which clears at 142 — 143° . An attempt to obtain a phenyl ester by heating a mixture of phenol and the acid with phosphorus oxychloride yielded two products in small quantity, melting at 122° and 151 — 152° respectively. No definite

product was obtained from the methyl ester by the action of ammonia, hydrazine, phenylhydrazine, or aniline.

Tetra-acetylquinic acid (Erwin and Koenigs, Abstr., 1889, 991) forms a crystalline *phenyl* ester, which melts at 167°. No well-defined chloride could be obtained by the action of thionyl chloride on the silver salt.

When quinic acid is heated at 130—140° with three times its weight of benzoyl chloride, *tetrabenzoylquinic acid*,



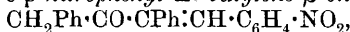
(only 1H₂O is lost at 95°; the *sodium* and *silver* salts contain 2 and 3H₂O respectively) is formed, together with a crystalline substance, C₂₈H₂₄O₉, melting at 107—108°, which probably is a *tribenzoylquinide* containing 1H₂O. The *ethyl* ester of tetrabenzoylquinic acid, melting at 134°, was prepared, and also the *chloride* in a crude state as a viscous oil. In pyridine solution, the reaction between benzoyl chloride

and quinic acid yields a *tribenzoylquinide*, $\text{C}_6\text{H}_7(\text{OBz})_3 \text{C} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{CO} \end{smallmatrix}$, melting at

148°, as the main product. When quinic acid is boiled with benzoyl chloride and a little zinc chloride, *dibenzoylquinol*, C₆H₄(OBz)₂, melting at 199°, is obtained, identical with the product of the benzoylation of quinol by the Schotten-Baumann method; below 135—140°, this product is not formed. Unlike the by-products, it is not soluble in ether; consequently its ready formation from quinic acid probably affords the most convenient means of detecting this acid.

By treating quinic acid with a solution of phosphoric oxide in (cooled) nitric acid of sp. gr. 1.5, a *product* was obtained which melted at 157°, contained nitrogen, and was acid in reaction. C. F. B.

Condensation of Dibenzyl Ketone with *p*-Nitro-, *p*-Hydroxy-, *p*-Chloro-, and *o*-Nitro-benzaldehydes. LEOPOLD SCHIMETSCHKE (*Monatsh.*, 1906, 27, 1—12. Compare Hertzka, Abstr., 1905, i, 291).—*Chloro-p-nitrobenzylidibenzyl ketone* (δ -chloro- $\alpha\gamma$ -diphenyl- δ -*p*-nitrophenyl- β -butanone), CH₂Ph·CO·CHPh·CHCl·C₆H₄·NO₂, formed by the action of hydrogen chloride on a benzene solution of dibenzyl ketone and *p*-nitrobenzaldehyde, cooled by ice, crystallises in matted, glistening, white needles, melts at 143°, is readily soluble in ether or benzene, but only sparingly so in methyl or ethyl alcohol, and remains unchanged on prolonged boiling or heating in a sealed tube at 100° with alcohol. The *phenylhydrazone*, C₂₈H₂₄O₉N₃Cl, crystallises in long, reddish-yellow prisms and melts at 168°. *p*-Nitrobenzylidenedibenzyl ketone [$\alpha\gamma$ -diphenyl- δ -*p*-nitrophenyl- $\Delta\gamma$ -butylene- β -one],



is formed when chloro-*p*-nitrobenzylidibenzyl ketone is heated at 165° under 14 mm. pressure; it crystallises from alcohol in colourless needles and melts at 104°.

Chloro-p-hydroxybenzylidibenzyl ketone [δ -chloro- $\alpha\gamma$ -diphenyl- δ -*p*-hydroxyphenyl- β -butanone], CH₂Ph·CO·CHPh·CHCl·C₆H₄·OH, formed by the action of hydrogen chloride on a mixture of dibenzyl ketone and *p*-hydroxybenzaldehyde dissolved in a small amount of glacial acetic acid, crystallises from ether in white plates, melts, decomposes, and resolidifies at 100°, and melts again at 138°.

p-Hydroxybenzylidenedibenzyl ketone [$\alpha\gamma$ -diphenyl- δ -*p*-hydroxyphenyl- $\Delta\gamma$ -butylene- β -one], $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CPh}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, is formed when chloro-*p*-hydroxybenzylidenedibenzyl ketone is boiled with methyl or ethyl alcohol or is heated in a vacuum at 145 — 150° ; it crystallises in colourless needles, melts at 139° , and is readily soluble in methyl or ethyl alcohol, but only sparingly so in benzene, toluene, or light petroleum.

Chloro-*p*-chlorobenzylidenedibenzyl ketone [δ -chloro- $\alpha\gamma$ -diphenyl- δ -*p*-chlorophenyl- β -butanone], $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CHPh}\cdot\text{CHCl}\cdot\text{C}_6\text{H}_4\text{Cl}$, formed from dibenzyl ketone and *p*-chlorobenzaldehyde, crystallises in white plates, melts at 169° , and remains unchanged when boiled with alcohol. When heated at 190° under reduced pressure, it yields hydrogen chloride and *p*-chlorobenzylidenedibenzyl ketone [$\alpha\gamma$ -diphenyl- δ -*p*-chlorophenyl- $\Delta\gamma$ -butylene- β -one], $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CPh}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Cl}$, which crystallises in white needles and melts at 128° .

When boiled with phenylhydrazine and acetic acid in alcoholic solution, dichlorobenzylidenedibenzyl ketone forms 1 : 4-diphenyl-5-*p*-chlorophenyl-3-benzylpyrazoline, $\text{NPh}\begin{matrix} \text{N}=\text{C}\cdot\text{CH}_2\text{Ph} \\ \text{CH}(\text{C}_6\text{H}_4\text{Cl})\cdot\text{CHPh} \end{matrix}$, which crystallises in long, white prisms, melts at 120 — 122° , and gives Knorr's pyrazoline reaction.

Chloro-*o*-nitrobenzylidenedibenzyl ketone [δ -chloro- $\alpha\gamma$ -diphenyl- δ -*o*-nitrophenyl- β -butanone], $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CHPh}\cdot\text{CHCl}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, formed from dibenzyl ketone and *o*-nitrobenzaldehyde, crystallises from benzene or alcohol in light yellow needles, melts at 176° , and remains unchanged when boiled with alcohol. The phenylhydrazone, $\text{C}_{23}\text{H}_{24}\text{O}_2\text{N}_3\text{Cl}$, crystallises in dark yellow prisms and decomposes at 142° .

When heated at 200° in a vacuum, chloro-*o*-nitrobenzylidenedibenzyl ketone yields hydrogen chloride, *o*-nitrobenzylidenedibenzyl ketone [$\alpha\gamma$ -diphenyl- δ -*o*-nitrophenyl- $\Delta\gamma$ -butylene- β -one], and traces of phenylacetyl chloride. G. Y.

Formation of Diazoxides and Naphthaquinoneanils from Nitrosobenzene. HANS EULER (*Ber.*, 1906, 39, 1035—1040).—

1 : 4-Naphthaquinoneanil, $\text{C}_6\text{H}_4\begin{matrix} \text{CO}—\text{CH} \\ \text{C}(\text{NPh})\text{CH} \end{matrix}$, is readily formed when an aqueous solution of α -naphthol, sodium hydroxide and ammonium chloride is added at 0° to a solution of nitrosobenzene in acetone. A small amount of a compound, $\text{C}_{22}\text{H}_{16}\text{ON}_2$, is formed at the same time (see following abstract). The anil crystallises from ether in large, ruby-red prisms and melts at 103° . It dissolves readily in most organic solvents and also in dilute acids, and is readily reduced by zinc and acetic acid to a leuco-compound, which is reoxidised when exposed to the air. The hydrochloride, $\text{C}_{16}\text{H}_{12}\text{ONCl}$, is insoluble in ether, and when freshly prepared is colourless, but rapidly darkens, and is hydrolysed by water. When boiled with dilute sulphuric acid, the anil is hydrolysed to aniline and 1 : 4-naphthaquinone. The anil is also formed by the action of hydroxylamine on a solution of α -naphthol and nitrosobenzene.

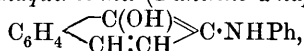
1 : 4-Naphthaquinone-*p*-toluidide, $\text{C}_{17}\text{H}_{13}\text{ON}$, prepared from nitrosotoluene, α -naphthol, and alkali, also crystallises in ruby-red prisms and

melts at 95°. A sparingly soluble compound melting at 176° is formed at the same time.

1 : 2-*Naphthaquinoneanil* is much less stable than the isomeric 1 : 4-compound, and must be immediately removed when once formed, as otherwise it is reduced to a leuco-compound. It crystallises from alcohol in slender, dark green needles, melts at 99—100°, and dissolves readily in most organic solvents. When hydrolysed, it yields aniline and β -naphthaquinone.

J. J. S.

Naphthaquinoneanils and their Derivatives. ASTRID EULER and HANS EULER (*Ber.*, 1906, 39, 1041—1045. Compare preceding abstract).—1 : 2-*Naphthaquinolanil* (2-anilino- α -naphthol),



is formed when the clear solution obtained by the action of α -naphthol, sodium hydroxide, and ammonium chloride dissolved in aqueous acetone on an acetone solution of nitrosobenzene is kept for two hours and then poured into water. It crystallises from benzene in colourless scales, melts at 156°, and is readily soluble in most organic solvents. It may also be obtained by reducing 1 : 2-naphthaquinoneanil.

The compound $\text{C}_{22}\text{H}_{16}\text{ON}_2$, obtained as a by-product in the preparation of 1 : 4-naphthaquinoneanil, is shown to be *anilino-1 : 4-naphthaquinoneanil*. It melts at 178—179°, is sparingly soluble, and, when hydrolysed with ethyl alcohol and fuming hydrochloric acid at 100°, yields aniline and anilinonaphthaquinone.

When the 1 : 4-naphthaquinoneanil is boiled in aqueous-alcoholic solution with hydroxylamine hydrochloride, it yields a small amount of α -naphthaquinoneoxime melting at 194°, a certain amount of *bis- α -naphthaquinoneoxime*, $\text{OH}\cdot\text{N}\cdot\text{C}_{10}\text{H}_5\text{O}\cdot\text{C}_{10}\text{H}_5\text{O}\cdot\text{N}\cdot\text{OH}$, which forms a red powder, melting above 300° and readily soluble in alkalis, and a considerable amount of *bis-1 : 4-naphthaquinoneanil*, $\text{C}_{32}\text{H}_{20}\text{O}_2\text{N}_2$, in the form of a purplish-red powder, melting at 233° and readily soluble in benzene.

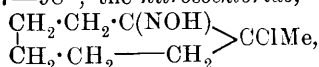
Nitrosophenol, α -naphthol, and alkali in acetone solution yield a small amount of a compound, $\text{C}_{16}\text{H}_{11}\text{O}_3\text{N}$, in the form of a minutely crystalline, brown powder, which does not melt below 300°.

J. J. S.

Terpenes and Ethereal Oils. LXXVII. New Heptacyclic Compounds. OTTO WALLACH (*Annalen*, 1906, 345, 139—154).—By the aid of Grignard's reaction, a number of heptacyclic compounds have been synthesised from suberone.

1-*Methylsuberol*, $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2 \end{array} \text{CMe}\cdot\text{OH}$, is obtained by the action of magnesium methyl iodide on suberone, and is a thick oil boiling at 183—185°, and having a sp. gr. 0.9285 and n_D 1.4677 at 22°. When heated with potassium hydrogen sulphate in a current of hydrogen, water is eliminated and Δ^1 -*methylsuberenone* (1-methyl- Δ^1 -cycloheptene), $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{CH} \\ \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2 \end{array} \text{CMe}$, is produced; it boils at 137.5—138.5°, and has a sp. gr. 0.824 and n_D 1.4581 at 19.5°; it is oxidised by dilute

potassium permanganate to ϵ -acetylhexoic acid, $\text{CH}_2\text{Ac}\cdot[\text{CH}_2]_4\cdot\text{CO}_2\text{H}$, which yields a *semicarbazone* melting at $113\text{--}114^\circ$ and is oxidised by sodium hypobromite to pimelic acid. The *nitrosate*, $\text{C}_8\text{H}_{14}\cdot\text{N}_2\text{O}_4$, melts and decomposes at $97\text{--}98^\circ$; the *nitrosochloride*,



melts at 106° . The nitrosochloride reacts with piperidine, giving the *nitrolamine*, $\text{C}_8\text{H}_4(\text{NO})\cdot\text{C}_5\text{NH}_{10}$, melting at 107° . The nitrosate and the nitrosochloride both react with sodium methoxide, the groups NO_3 or Cl being replaced by OMe , *methoxymethylsuberaneoxime* being formed; the latter crystallises in plates melting at $74\text{--}75^\circ$, and when boiled with acids yields a ketone resembling suberone in odour.

Methylsuberone, $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{CO} \\ \text{CH}_2\cdot\text{CH}_2\cdot\text{CH} \end{array} > \text{CMe}$ or $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{CO} \\ \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2 \end{array} > \text{C}\cdot\text{CH}_2$, is

prepared from methylsuberene nitrosochloride, from which the hydrochloric acid is eliminated by means of a tertiary base, dimethylaniline; it is purified by conversion into the *semicarbazone*, which melts at $162\text{--}163^\circ$, boils between 200° and 205° , and has a sp. gr. 0.9695 and n_D 1.4867 at 21° . When reduced with sodium and alcohol, a saturated alcohol is obtained, which is oxidised by chromic acid to

methylsuberone (1-methylcycloheptane-2-one), $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{CO} \\ \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2 \end{array} > \text{CHMe}$,

which was obtained in the form of its *semicarbazone* melting at $129\text{--}131^\circ$.

Methylenesuberene, $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2 \end{array} > \text{C}\cdot\text{CH}_2$, is obtained from ethyl

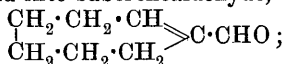
suberolacetate (Abstr., 1901, i, 156), which is hydrolysed to subereneacetic acid; on heating, this substance loses carbon dioxide, yielding the methylenesuberene, which resembles very closely the isomeric Δ^1 -methylsuberene, above described. Methylenesuberene shows little tendency to absorb oxygen from the air. When oxidised with potassium perman-

ganate, suberone and the *glycol*, $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2 \end{array} > \text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, are formed; the latter forms a colourless, crystalline solid which melts at $50\text{--}51^\circ$ and boils at $135\text{--}140^\circ$ under 16 mm. pressure.

When treated with dilute acids, water is immediately eliminated, and a saturated *suberanealdehyde*, $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2 \end{array} > \text{CH}\cdot\text{CHO}$, produced; it is an oil smelling like benzaldehyde, and forms a *semicarbazone* melting at $153\text{--}154^\circ$ and a solid *oxime* boiling at $110\text{--}120^\circ$ under 11 mm. pressure. The aldehyde is oxidised by silver oxide to heptamethylenecarboxylic acid.

In the oxidation of methylenesuberene by potassium permanganate, *hydroxysuberanecarboxylic acid*, $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2 \end{array} > \text{C}(\text{OH})\cdot\text{CO}_2\text{H}$, is formed together with the glycol; it melts at 78° and is identical with the acid formed from suberonecyanohydrin and from bromocycloheptanecarboxylic acid; it can be readily purified by means of a well-characterised sodium salt and when warmed with lead peroxide and

sulphuric acid is converted into suberone. Methylene-suberene yields a *nitrosochloride* with ethyl nitrite and hydrochloric acid; the compound is not formed so readily as in the case of Δ^1 -methylsuberene; it is converted by sodium methoxide into a liquid *oxime*, which is decomposed by sulphuric acid into suberenaldehyde,

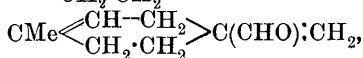


its *semicarbazone* crystallises in needles melting at 203—204°. The constitution of the aldehyde was fixed by oxidising it with silver oxide to suberenecarboxylic acid (m. p. 50—51°). K. J. P. O.

Terpenes and Ethereal Oils. LXXVI. New Compounds from β -Terpineol. OTTO WALLACH [with ERNST SCHMITZ] (*Annalen*, 1906, 345, 127—138).— β -Terpineol, $\text{OH} \cdot \text{CMe} \langle \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \rangle \text{CH} \cdot \text{CMe} \cdot \text{CH}_2$, has been shown (Abstr., 1902, i, 803) to combine with nitrosyl chloride, nitrogen peroxide, and nitrogen trioxide. The reactions of these substances have now been studied.

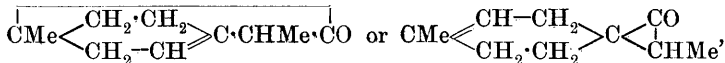
With sodium methoxide, the nitrosochloride yields a *hydroxyoxime*, which could not be obtained in a definite crystalline condition; when boiled with acids, hydroxylamine is eliminated, and a *compound*, $\text{C}_{10}\text{H}_{14}\text{O}$, which is either an aldehyde or ketone according to the origin of the hydroxyoxime, produced.

The *aldehyde*, $\text{CMe} \langle \begin{array}{c} \text{CH}-\text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \rangle \text{C} \cdot \text{CMe} \cdot \text{CHO}$,



or $\text{CMe} \langle \begin{array}{c} \text{CH}-\text{CH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \rangle \text{C} \cdot \text{CHMe} \cdot \text{CHO}$, which is the first aldehyde of the terpene series to be synthesised, is prepared by heating the product of the action of sodium methoxide on the nitrosochloride with a saturated solution of oxalic acid; the *semicarbazone* is then prepared and crystallises in leaflets melting at 209°. From the latter, the aldehyde is regenerated by hydrolysis with oxalic acid. It boils at 96° under 11 mm. pressure, and has a sp. gr. 0.97 and n_D 1.4952 at 19°; it reduces silver nitrate, being oxidised to an *acid*, $\text{C}_{10}\text{H}_{14}\text{O}_2$, which crystallises in leaflets melting at 74°. Its *silver* salt, $\text{C}_{10}\text{H}_{13}\text{O}_2\text{Ag}$, was analysed.

The *ketone*,

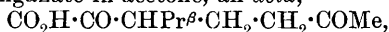


is prepared by hydrolysing the hydroxyoxime with 10 per cent. sulphuric acid instead of oxalic acid, and is purified by conversion into a *semicarbazone* which forms crystals melting at 218°; the latter is converted into the ketone by warming with strong sulphuric acid; it is an oil boiling at 93° under 13 mm. and at 218—220° under the ordinary pressure. It has a sp. gr. 1.001 and n_D 1.4937 at 20°. With hydroxylamine, it yields a solid *oxime* melting at 124—125°. It does not reduce an ammoniacal silver solution, but decolorises bromine and potassium permanganate immediately. K. J. P. O.

Buchu-camphor (Diosphenol), $C_{10}H_{16}O_2$. FRIEDRICH W. SEMMLER and MCKENZIE (*Ber.*, 1906, **39**, 1158—1170. Compare Shimoyama, *Abstr.*, 1888, 1205; Kondakoff and Bjalobrezski, *Abstr.*, 1897, i, 227 and 443; Kondakoff and Bachtschéeff, *Abstr.*, 1901, i, 334).—Diosphenol, $C_{10}H_{16}O_2$, obtained from oil of buchu leaves, appears from the following facts to have the structure $CHPr^{\beta} \begin{smallmatrix} \text{CH}_2-\text{CH}_2 \\ \text{CO}\cdot\text{C}(\text{OH}) \end{smallmatrix} \text{CMe}$; it melts when pure at 83—84°, boils at 109—110° under 10 mm. pressure, and is optically inactive.

On reduction with sodium and alcohol, it gives *p-menthane-2:3-diol*, $CHPr^{\beta} \begin{smallmatrix} \text{CH}_2-\text{CH}_2 \\ \text{CH}(\text{OH})\cdot\text{CH}(\text{OH}) \end{smallmatrix} \text{CHMe}$, which boils at 135—137° under 10 mm. pressure, has a sp. gr. 0.981 at 20°, and n_D 1.47593; on oxidation with chromic acid, the diol gives a *keto-alcohol*, $C_{10}H_{18}O_2$, which boils at 105—115° under 13 mm. pressure, has a sp. gr. 0.968 at 20°, n_D 1.4616, gives a *semicarbazone* melting at 200°, and when oxidised with potassium permanganate gives α -methyl- δ -isopropyladipic acid, melting at 104°. With bromine in glacial acetic acid, diosphenol gives a *dibromo-derivative*, $C_{10}H_{14}Br_2O_2$, and when heated with concentrated hydrochloric acid for two hours at 150—180° it gives thymol nearly quantitatively, a little carvacrol being also formed.

On oxidising diosphenol with ozone in presence of water, γ -acetyl- α -isopropyl-*n*-butyric acid, $CH_2Ac\cdot CH_2\cdot CHPr^{\beta}\cdot CO_2H$, is obtained quantitatively, the product being identical with the acid obtained by Semmler (*Abstr.*, 1904, i, 261) and Wallach (*Abstr.*, 1903, i, 566); it melts at 41°, boils at 165° under 14 mm. pressure, has a sp. gr. 1.041 at 20°, n_D 1.45862, and a mol. refraction 45.2 (calc. for a keto-acid, $C_9H_{16}O_3$, 45.6). An alkaline solution of bromine converts γ -acetyl- α -isopropyl-*n*-butyric acid into α -isopropylglutaric acid, which melts at 94.5° and boils at 202—205°. When diosphenol is oxidised with potassium permanganate in acetone, an *acid*,

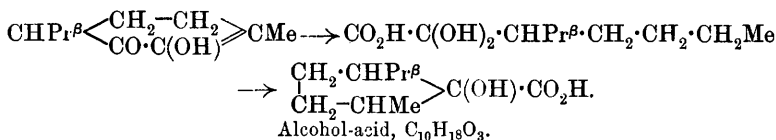


is the first product, but this on distillation in a vacuum loses water and gives an *acid*, $CO_2H\cdot C \begin{smallmatrix} \text{CHPr}^{\beta}\cdot\text{CH}_2 \\ \text{CH}-\text{CO} \end{smallmatrix} \text{CH}_2$; the latter crystallises from water in plates, melts at 104—105°, boils at 187—193° under 14 mm. pressure, has a sp. gr. 1.0767 at 20°, n_D 1.47936, and a mol. refraction 47.96 (calc. for the keto-acid, $C_{10}H_{14}O_4$, 47.52). The *oxime*, $C_{10}H_{15}O_3N$, melts at 182°.

The proximity in diosphenol of the hydroxyl group to the carbonyl group modifies the properties of the latter very considerably; diosphenol does not give a semicarbazone nor a phenylhydrazone, although it gives a normal *oxime*, $C_{10}H_{17}O_2N$, melting at 125° (Kondakoff describes the oxime as melting at 156°). Diosphenol behaves, moreover, like an aldehyde with regard to the magenta test and towards Fehling's solution and ammoniacal silver nitrate.

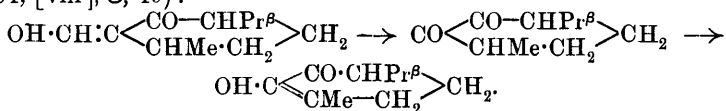
With boiling acetic anhydride containing sodium acetate, diosphenol gives an *acetyl* derivative, $C_{12}H_{18}O_3$, which boils at 138—143° under 13 mm. pressure, has a density 1.034 at 20°, and n_D 1.4848. The *benzoyl* derivative, $C_{17}H_{20}O_3$, boils at 218—219° under 11 mm. pressure, and the *phenylurethane* melts at 41°.

On heating diosphenol with alcoholic potassium hydroxide at 150—160°, the following changes occur :



The *alcohol-acid*, $\text{C}_{10}\text{H}_{18}\text{O}_3$, crystallises from water in needles, melts at 94°, and boils at 167—168° under 14 mm. pressure; the *methyl ester*, $\text{C}_{11}\text{H}_{20}\text{O}_3$, boils at 104—105° under 13 mm. pressure, has a sp. gr. 1·0008 at 20°, and n_D 1·45512. The *ethyl ester*, $\text{C}_{12}\text{H}_{22}\text{O}_3$, boils at 120° under 12 mm. pressure, has a sp. gr. 0·984 at 20°, and n_D 1·45162. The *acetyl derivative*, $\text{C}_{14}\text{H}_{24}\text{O}_4$, of the ethyl ester boils at 125—130° under 9 mm. pressure, has a sp. gr. 1·01 at 20°, and n_D 1·45112. On oxidising the alcohol-acid, $\text{C}_{10}\text{H}_{18}\text{O}_3$, with lead peroxide in presence of acid, the ketone, $\begin{array}{c} \text{CH}_2\cdot\text{CHPr}^\beta \\ \text{CH}_2\text{---CHMe} \end{array} \text{CO}$ (Semmler's *dihydrocamphorophorone*, Wallach's *dihydropulegenone*), is obtained; it boils at 64—65° under 12 mm. pressure, has a sp. gr. 0·893 at 20°, n_D 1·4446, and gives a *semi-carbazone*, $\text{C}_{10}\text{H}_{19}\text{ON}_3$, melting at 195°. When the acid, $\text{C}_{10}\text{H}_{18}\text{O}_3$ is heated with hydrochloric acid at 150—160°, it gives rise to a *compound*, $\text{C}_9\text{H}_{18}\text{O}$, which boils at 63° under 14 mm. pressure, has a sp. gr. 0·893 at 20°, and n_D 1·44862.

Diosphenol was obtained synthetically from hydroxymethylenementhone according to the stages (compare Martine, *Ann. Chim. Phys.*, 1904, [viii], 3, 49):



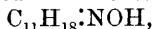
Hydroxymethylenementhone is oxidised, best by ozone in presence of water, to the diketone, this undergoing change under the influence of acid into the enolic form, diosphenol. *Hydroxymethylenementhone* boils at 120° under 11 mm. pressure, has a sp. gr. 0·994 at 20°, n_D 1·49668, mol. refraction 53·6 (calc. for a keto-alcohol, 52·03, for a di-alcohol, 52·89). W. A. D.

Carvone. II. Action of Magnesium Methyl Iodide on Carvone.

HANS RUPE and KARL LIECHTENHAN (*Ber.*, 1906, 39, 1119—1126. Compare Abstr., 1905, i, 449).—The action of carvone on an ethereal solution of magnesium methyl iodide leads to the formation of a *hydrocarbon*, $\text{C}_{11}\text{H}_{16}$, which boils at 195—197° under 745·5 mm. pressure and at 72·5—74° under 9·5 mm., has a sp. gr. 0·8728, n_D 1·5007, $[\alpha]_D + 70\cdot38^\circ$, all at 20°, and forms only a tetrabromo-additive compound, although the molecular refraction requires the presence of three ethylenic linkings. The substance combines quantitatively with hydrogen ferricyanide and also with hydrogen ferrocyanide and hydrogen cobalticyanide, but in none of these cases can the pure hydrocarbon be regenerated. It is reduced by sodium and amyl alcohol to a *dihydro-derivative*, $\text{C}_{11}\text{H}_{18}$, which boils at 193—195° under 745 mm.

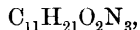
pressure, has a sp. gr. 0.8594, and $[\alpha]_D - 27.18^\circ$ at 20° , and molecular refraction 50.11.

Methyl dihydrocarvone, $C_{11}H_{18}O$, occurs as a by-product in the preparation of the hydrocarbon. It is separated in the form of the oxime, and, after purification by conversion into the semicarbazone, is obtained as a colourless oil which has the odour of dihydrocarvone, boils at $102-103.5^\circ$ under 11 mm. pressure, and has a sp. gr. 0.9270 and $n_D 1.48157$ at 20° . Evidence is obtained which points to the possibility of the substance being a mixture of two isomerides. The *oxime*,



separates from dilute alcohol in glassy prisms and melts at $135-136^\circ$. The *semicarbazone*, $C_{12}H_{21}ON_3$, crystallises from methyl alcohol in hexagonal leaflets and melts at $180-181^\circ$.

8-Hydroxytetrahydrocarvone is obtained when dihydrocarvone is shaken with 40 per cent. sulphuric acid for twenty-four hours (compare Wallach, Abstr., 1893, i, 595; Baeyer, Abstr., 1894, i, 535). The *oxime*, $C_{10}H_{18}O \cdot NOH$, obtained by the action of hydroxylamine hydrochloride in the presence of sodium hydrogen carbonate, is somewhat easily soluble in water; it separates from dilute alcohol in thick, glistening crystals and melts at $120-121^\circ$. The *semicarbazone*,



separates from methyl alcohol in large crystals and, when heated very slowly, softens at 150° and melts at $157-158^\circ$ (compare Baeyer and Henrich, Ber., 1895, 28, 1590; Knoevenagel and Samel, Abstr., this vol., i, 296).

8-Hydroxytetrahydrocarvone, which by distillation with steam in the presence of 20 per cent. sulphuric acid is converted into carvenone, is reduced by sodium and alcohol to α -2:8-dihydroxyterpane (compare Abstr., 1905, i, 449). C. S.

Pinene Hydrochloride and Camphene Hydrochloride. ALBERT HESSE (Ber., 1906, 39, 1127-1155).—The author discusses the evidence brought forward by Wagner and Bryckner (Abstr., 1900, i, 46) in support of their contention that pinene hydrochloride is bornyl chloride and camphene hydrochloride *isobornyl* chloride, and points out its insufficiency; the facts given below, however, prove that Wagner's speculations in this direction were correct.

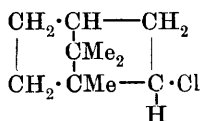
Attempts to bring about the interaction of pinene or camphene hydrochloride with magnesium according to Grignard's method, using the ordinary catalytic agents (iodine, aluminium chloride, alkyl haloids), were unsuccessful; but by adding the hydrochloride dissolved in benzene and ether to magnesium while the latter is acting vigorously on ethyl bromide dissolved in ether, a magnesium compound, $C_{10}H_{17} \cdot MgCl$, is produced; in this case, magnesium ethyl bromide acts as a catalyst. With pinene hydrochloride, a yield of 80-85 per cent. of the magnesium compound is obtained, whilst 10-15 per cent. of the hydrochloride is converted into a *d-hydrodicamphene*, $(C_{10}H_{17})_2$, which crystallises from glacial acetic acid, melts at $85-87^\circ$, and has $[\alpha]_D + 28.42'$ in 20 per cent. benzene solution; small quantities of camphene and camphane are also formed. From camphene hydrochloride, 60 per cent. of the compound $C_{10}H_{17} \cdot MgCl$ is produced, with

about 20 per cent. of a *hydrodicamphene*, $C_{20}H_{34}$, which is perhaps identical with the *d*-hydrodicamphene formed from pinene hydrochloride; it melts, however, at $90-91^\circ$, has $[\alpha]_D + 2^\circ 37'$, and may be a mixture.

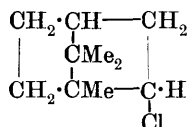
The same inactive camphane melting at 153° is obtained by decomposing with water the magnesium derivative of either active or inactive pinene hydrochloride or active or inactive camphene hydrochloride. On passing dry air or oxygen into the ethereal solution of the magnesium compound prepared from pinene hydrochloride and decomposing the product with dilute acid, a 65—85 per cent. yield of borneol is obtained; the remainder of the product consists principally of hydrodicamphene, with a small quantity of camphane and camphene; in some cases, 5—8 per cent. of *isoborneol* is obtained, formed partly from camphene hydrochloride present as an impurity in the pinene hydrochloride. From *l*-pinene hydrochloride ($[\alpha]_D - 26^\circ 3'$), an *l*-borneol melting at $208-209^\circ$ and having $[\alpha]_D - 11^\circ 6'$ was obtained in one experiment; in another experiment, the *l*-borneol on crystallisation from light petroleum gave fractions with $[\alpha]_D$ varying from -7° to -3° . The rotatory power of the *l*-borneol thus obtained is therefore much smaller than that of natural *l*-borneol.

On oxidising the magnesium derivative of camphene hydrochloride in a similar manner, the product consists of about 30 per cent. of borneol, 15 per cent. of *isoborneol*, 21 per cent. of hydrodicamphene, and 34 per cent. of camphene and camphane. The production of so large a proportion of borneol is remarkable, and indicates either that in the preparation of the magnesium compound of camphene hydrochloride a considerable amount of the magnesium derivative of pinene hydrochloride is produced, or that during the oxidation of the magnesium compound isomeric change occurs.

Details are given of the methods used in determining the approximate composition of the various mixtures dealt with. The conclusions drawn from the data given above are (1) that pinene hydrochloride is bornyl chloride, and camphene hydrochloride *isobornyl* chloride; (2) that these hydrochlorides are stereoisomeric, as shown in the formulæ:

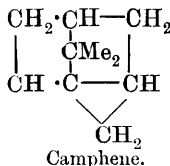


Pinene hydrochloride
(bornyl chloride).



Camphene hydrochloride
(*isobornyl* chloride).

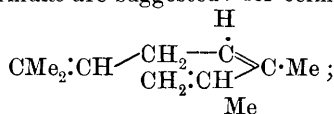
(3) that borneol and *isoborneol* are stereoisomeric secondary alcohols corresponding with the stereoisomeric chlorides; (4) that the formula of camphene is probably



W. A. D.

Ocimene and Myrcene. C. J. ENKLAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 8, 714—723. Compare van Romburgh, *Abstr.*, 1901, i, 220; Semmler, *Abstr.*, 1901, i, 732; Chapman, *Trans.*, 1903, 83, 505).—Ocimene boils at 81° under 30 mm. pressure, or at 172·5° under atmospheric pressure, and has the sp. gr. 0·8031 at 15° and n_D 1·4857 at 18°. *alloOcimene*, formed when ocimene is boiled under atmospheric pressure, boils at 81° under 12 mm. or at 188° under 750 mm. pressure, has the sp. gr. 0·8182 at 15° and n_D 1·5296, and absorbs oxygen and resinifies even more quickly than does ocimene. Ocimene and *alloocimene* are stable at the ordinary temperature, although the latter polymerises when exposed to light. Myrcene polymerises slowly at the ordinary temperature. The end-point of the absorption of bromine by ocimene and by *alloocimene* cannot be observed accurately, but the amount absorbed points to the presence of three ethylene linkings. On reduction with sodium and alcohol, myrcene, ocimene, and *alloocimene* yield the same *dihydro-ocimene*, which boils at 166—168° under 761 mm. pressure, has the sp. gr. 0·7792 at 15° and n_D 1·4507 at 17°, and forms a *dibromide*; this separates from methyl alcohol in snow-white crystals and melts at 88°. In the presence of nickel at 180°, dihydro-ocimene absorbs hydrogen, forming a colourless liquid ($\beta\zeta$ -dimethyloctane?), which boils at a much lower temperature than dihydro-ocimene.

The following formulæ are suggested: for ocimene,



for *alloocimene*, $\text{CMe}_2\text{:CH}-\text{CH}_2\cdot\text{C}=\dot{\text{C}}-\text{CH}$; and for myrcene,

$\text{CMe}_2\text{:CH}-\text{CH}_2\cdot\text{CH}_2 > \text{C}\cdot\text{CH}_2$, dihydro-ocimene having the constitution $\text{CMe}_2\text{:CH}-\text{CH}_2\cdot\text{CH}_2 > \text{CHMe}$.

G. Y.

Aliphatic Terpene Alcohols. C. J. ENKLAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 8, 723—727. Compare preceding abstract).—When digested with glacial acetic acid and dilute sulphuric acid at 50—60°, ocimene yields 10 per cent. of its weight of *ocimenol*, $\text{C}_{10}\text{H}_{18}\text{O}$, which boils at 97° under 10 mm. pressure, and has the sp. gr. 0·901 at 15° and n_D 1·4900 at 15°. It forms a *phenylurethane*, $\text{C}_{17}\text{H}_{23}\text{O}_2\text{N}$, which crystallises in white needles and melts at 72°.

Myrcenol (Barbier, *Abstr.*, 1901, i, 477) is obtained from myrcene in a yield of about 20 per cent. of the theoretical; it forms a *phenylurethane*, $\text{C}_{17}\text{H}_{23}\text{O}_2\text{N}$, which melts at 68°.

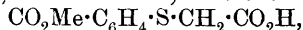
The phenylurethane of linalool, prepared according to Wahlbaum and Hüthig's directions (*Abstr.*, 1903, i, 506), is obtained in a yield of 85 per cent. of the theoretical if the process is prolonged for three months. The product consists of a mixture of the racemic with the optically active urethane, which melts at 66° and has a rotation of

23°27' in a 200 mm. tube; from this the rotation of pure optically active linalool is calculated as 35°27'.

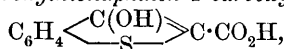
A mixture of the phenylurethanes of myrcenol and *r*-linalool melts at 60—62°. G. Y.

Sugar Components of the Glucosides Solanin, Conval-lamarin, and Scammonin. EMIL VOTOČEK and RUDOLF VONDRÁČEK (*Zeit. Zuckerind. Böhm.*, 1905, 30, 117—120. Compare Abstr., 1905, i, 74).—On hydrolysis, both solanin and convallamarin yield *d*-galactose in addition to other sugars. Similarly, scammonin yields at least rhodose and dextrose, so that the name scammonose represents a mixture and should not be used. T. H. P.

Sulphur Analogues of the Indigotin Group. PAUL FRIEDLÄNDER (*Ber.*, 1906, 39, 1060—1066. Compare Friedländer and Mauthner, Abstr., 1905, i, 102).—*o*-Carboxyphenylthioglycollic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, prepared from thiosalicylic acid, alkali, and chloroacetic acid, melts at 213°; its *monomethyl* ester,



melts at 151°, whilst its *dimethyl* ester melts at 52°. *o*-Carboxyphenylthioglycollic acid, when acted on by alkalis, forms *thioindoxyl-carboxylic acid* [*2-hydroxythionaphthen-1-carboxylic acid*],



which readily loses carbon dioxide to form *thioindoxyl* [*2-hydroxythionaphthen*], $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{C}(\text{OH}) \\ \text{S} \end{smallmatrix}\rangle\text{CH}$, which crystallises in needles, melts at 71°, and readily assumes a red tint on exposure to the atmosphere. On the addition of potassium ferricyanide to its solution in sodium hydroxide, the *dye*, $\text{C}_{16}\text{H}_8\text{O}_2\text{S}_2$, separates in red flakes. It is assumed that the latter substance has a structure analogous with that of indigotin. It crystallises from xylene in needles with a bronze lustre; its solution in chloroform is fluorescent; at a high temperature, it is more stable than indigotin; it sublimes in needles, and in small amounts can be distilled without undergoing decomposition; it is very stable towards oxidising agents.

Thioindoxyl is also analogous to indoxyl; it is readily oxidised to a dye; it readily combines with aromatic aldehydes, ketones, and diketones to form thioindogenides.

Thioindoxylcarboxylic acid, like indoxylcarboxylic acid, readily loses carbon dioxide, and is characterised by the difficulty with which its ester is saponified.

The preparation of various other compounds is indicated, details of which are promised in a subsequent paper. A. McK.

Alkaloids of *Anagiris foetida*. G. GOESSMANN (*Arch. Pharm.*, 1906, 244, 20—24. Compare Schmidt, Litterscheid, and Klostermann, Abstr., 1900, i, 513).—The crude alkaloids were prepared from the seeds by the method of Partheil and Spasski (Abstr., 1896, i, 657). They were converted into phenylthiocarbamides by allowing them to

remain in alcoholic solution with phenylthiocarbimide. The solid cytisine derivative was filtered off, and from the filtrate (by evaporation, heating of the residue with dilute hydrochloric acid, and further treatment) an alkaloid, or mixture of alkaloids, "anagyryne," was obtained; this is resinous, boils at 245° under 30 mm. pressure, and contains C 72.4, H 8.68, N 11.68 per cent., which does not accord well with the formula $C_{15}H_{22}ON_2$; it forms 65 per cent. of the crude alkaloids.

The cytisine can be regenerated from its phenylthiocarbimide by heating the latter with concentrated hydrochloric acid at 150° .

C. F. B.

Cocaine Formate. FERD. VIGIER (*J. Pharm. Chim.*, 1906, [vi], 23, 97—98).—This salt, prepared by adding formic acid (1 mol.) to cocaine (1 mol.) suspended in water, crystallises from water in colourless, silky needles, melts at about 42° , dissolves in 41 parts of water and in 2.3 parts of alcohol at 20° , and has $[\alpha]_D - 56.40'$ in water at the same temperature. The salt possesses a slightly bitter taste: it is hydrolysed by water at 90° .

T. A. H.

Alkaloids from Species of Datura which induce Mydriasis. ERNST SCHMIDT (*Arch. Pharm.*, 1906, 244, 66—71. Compare Abstr., 1905, i, 717).—The seeds of a variety of *Datura fastuosa*, designated *flor. cœrul. plen.*, were found to contain 0.22 per cent. scopolamine and 0.034 hyoscyamine, whilst those of a variety designated *flor. alb. plen.* contained 0.20 and 0.023 per cent. respectively, a little atropine being present in both cases. *D. fastuosa* is thus certainly not identical with *D. alba* (Shimoyama and Koshima, *Apoth. Zeit.*, 1892, 458).

[With ADOLF KIRCHER.]—In the seeds of *D. arborea*, procured from abroad, scopolamine and hyoscyamine were found in the proportion 1 : 4. The other parts of a plant grown in Marburg, several years old and in flower when gathered, had been found to contain mainly scopolamine (*loc. cit.*). The stem of a younger plant, however, grown in Marburg and gathered after it had flowered, contained mainly hyoscyamine; yet the root of this plant contained but little hyoscyamine.

C. F. B.

Sparteine Alkylhaloids. MAX SCHOLTZ (*Arch. Pharm.*, 1906, 244, 72—77. Compare Abstr., 1904, i, 1045).—The statement made previously, that different compounds are obtained by the successive addition to sparteine of two different alkylhaloids in different order, is erroneous.

Sparteine forms a *benzyl iodide*, $C_{15}H_{26}N_2 \cdot CH_2PhI$, melting at 168° , by simple addition at the ordinary temperature.

A quaternary *platinichloride*, $C_6H_4 \begin{smallmatrix} <CH_2> \\ <CH_2> \end{smallmatrix} C_{15}H_{26}N_2PtCl_6$, melting and decomposing at 218° , can be obtained from the additive product of sparteine with *o*-xylylene bromide, and another, $C_{15}H_{26}N_2Me_2PtCl_6$, from the additive compound obtained by heating sparteine with excess of methyl iodide at 180 — 190° .

C. F. B.

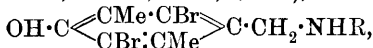
Hydroxybenzylpiperidines and Dibromo-*p*-hydroxy- ψ -cumyl-anilines. KARL AUWERS and A. DOMBROWSKI (*Annalen*, 1906, 344, 280—299. Compare Hildebrandt, *Abstr.*, 1900, ii, 676; 1905, i, 80).—Hydroxybenzylpiperidines are formed by the simultaneous action of formaldehyde and secondary amines on phenols, which contain either an *o*- or a *p*-hydrogen atom, in aqueous-alcoholic solution. The following new substances, $C_5NH_{10}\cdot CH_2R$, are described.

From *m*-cresol, $R = p\text{-hydroxy-o-methylphenyl}$: large, glistening prisms, melts at 57° , and is moderately soluble in water. From *v*-o-xyleneol, $R = 4\text{-hydroxy-2:3-dimethylphenyl}$: an oil, which forms a crystalline hydrochloride. From *v*-*m*-xyleneol, $R = 4\text{-hydroxy-3:5-dimethylphenyl}$: stout needles, melts at $117.5\text{--}118.5^\circ$, and is slightly soluble in water. From *s*-*m*-xyleneol, $R = 4\text{-hydroxy-2:6-dimethylphenyl}$: large, transparent needles, melts at 98.5° , and is only sparingly soluble in water. From *p*-xyleneol, $R = 4\text{-hydroxy-2:5-dimethylphenyl}$: slender, white needles, melts at $131.5\text{--}132^\circ$, and is almost insoluble in water. From ψ -cumenol, $R = 2\text{-hydroxy-3:5:6-trimethylphenyl}$: nacreous scales or large, hexagonal plates, melts at $69\text{--}70^\circ$, and is almost insoluble in water. From guaiacol, $R = 3\text{-methoxy-4-hydroxyphenyl}$: stout needles, melts at $99.5\text{--}100.5^\circ$. From *o*-nitrophenol, $R = 3\text{-nitro-4-hydroxyphenyl}$: iridescent, red needles, melts at $140\text{--}141.5^\circ$, and is sparingly soluble in water.

The hydroxybenzylpiperidines are almost all soluble in the usual organic solvents except in petroleum, only the derivatives of thymol, carvacrol, and the naphthols are less readily soluble. Those which are more or less soluble in water are correspondingly volatile in a current of steam.

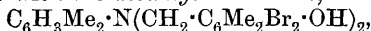
The substance $C_6H_4 \begin{smallmatrix} \text{C}(\text{CH}_2 \cdot \text{NMe}_2) \\ \text{CH} = \text{CH} \end{smallmatrix} > \text{C} \cdot \text{OH}$, formed by the action of dimethylamine and formaldehyde on β -naphthol, crystallises in small leaflets and melts at $74\text{--}75^\circ$.

The following derivatives of dibromo-*p*-hydroxy- ψ -cumylaniline (Auwers and Marwedel, *Abstr.*, 1896, i, 149),

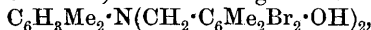


are formed by the action of dibromo-*p*-hydroxy- ψ -cumyl bromide on the base in ethereal solution.

From *o*-toluidine, $R = C_6H_4Me$: white, fine crystalline powder, m. p. $154\text{--}154.5^\circ$. From *m*-toluidine, $R = C_7H_7$: white, crystalline powder, m. p. $123.5\text{--}125^\circ$. From *p*-toluidine, $R = C_7H_7$: small, stout prisms, m. p. $96\text{--}98^\circ$. From *as*-*o*-xylidine, $R = C_6H_3Me_2$: slightly yellow powder, m. p. 120° . From *v*-*o*-xylidine, $R = C_6H_3Me_2$: slightly red, fine crystalline powder, m. p. 158° . From *as*-*m*-xylidine, $R = C_6H_3Me_2$: slender needles, m. p. $144.5\text{--}145.5^\circ$. From *v*-*m*-xylidine, $R = C_6H_3Me_2$: white, crystalline powder, m. p. $144.5\text{--}146^\circ$; is formed together with the *dicumyl* derivative,



which is obtained as a white, sparingly soluble, crystalline powder melting at $207\text{--}208^\circ$. From *s*-*m*-xylidine, $R = C_6H_3Me_2$: slender needles, m. p. $153.5\text{--}155^\circ$; is formed together with



melting at 213—214°. From *p*-xylidine, $R = C_6H_3Me_2$: slender needles, melts at 155·5—157°. From ψ -cumidine, $R = C_6H_2Me_3$: small, glistening needles and prisms, m. p. 140—141·5°. G. Y.

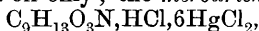
Physical Constants of Pure Pyridine. JAN VON ZAWIDZKI (*Chem. Zeit.*, 1906, 25, 299).—Two samples of pyridine, purified by repeated fractional distillation and drying with solid sodium hydroxide, were found to solidify at 42°. Altschal and Schneider (*Abstr.*, 1895, ii, 206) state that pyridine does not solidify when cooled to -200° . The two samples gave the following values: boiling point, $115\cdot1^\circ$ and $115\cdot3^\circ$ under normal pressure; sp. gr. 0·97794 and 0·97796 at $25^\circ/4^\circ$, and n_D 1·50700 and 1·50729 at 25° . P. H.

Etherification of 4-Pyridones with Diazo-derivatives of Aliphatic Hydrocarbons. ALBERTO PERATONER and E. AZZARELLO (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 139—144).—When 4-pyridone is etherified by means of diazomethane or diazoethane, the alkyl residue enters both the NH-group and also the hydroxy-group of the tautomeric hydroxypyridine. This affords an exception to von Pechmann's rule, which states that, with tautomeric substances, the methyl derivative obtained is mainly that corresponding with the form possessing the most marked acid character.

4-Ethoxypyridine, $OEt \cdot C \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \text{CH} \cdot \text{CH} \end{smallmatrix} \text{N}$, is a colourless liquid which has an odour resembling that of pyridine, boils at 96° under 15 mm. pressure, and is miscible with alcohol. T. H. P.

Action of Formaldehyde on α -Picoline (2-Methylpyridine). ANDREAS LIPP and E. ZIRNGIBL (*Ber.*, 1906, 39, 1045—1054. Compare Lipp and Richard, *Abstr.*, 1904, i, 342).—Trimethylol-2-picoline, $C_5NH_4 \cdot C(CH_2 \cdot OH)_3$, is formed, together with the corresponding mono- and dimethylol compounds, when 2-picoline is heated with 40 per cent. formaldehyde for twenty-seven hours at 135—140°. Better yields may be obtained by heating the dimethylol compound in a similar manner. It is most readily separated from the dimethylol compound by means of the mercurichloride, which is more readily soluble in water than the corresponding salt of dimethylol-2-picoline.

Trimethylol-2-picoline crystallises from chloroform or dry ether in colourless needles, melts at 68° , and begins to decompose at 170° . It dissolves readily in water to an alkaline solution. The hydrochloride has been obtained as an oil only; the mercurichloride,



crystallises from hot water in colourless, glistening prisms, melting at 138° and readily soluble in cold alcohol; the platinichloride crystallises in quadratic plates, decomposes at 167—168°, and is insoluble in absolute alcohol; the aurichloride forms yellow prisms melting at 140° , and the picrate yellow prisms melting at $111\cdot5$ — $112\cdot5^\circ$, and only sparingly soluble in cold water. Trimethylol-2-picoline methochloride is an oil and is readily soluble in water or alcohol. It yields a mercurichloride, $C_{10}H_{16}O_3NCl \cdot 6HgCl_2$, which crystallises in short, glistening

prisms melting at 152—153°; a *platinichloride* crystallising in needles and decomposing at 151°, and an *aurichloride* melting at 138—140°.

Trimethylol-2-picoline tribenzoate, $C_5NH_4 \cdot C(CH_2 \cdot OBz)_3$, crystallises from methyl alcohol in needles melting at 94°, and yields a *platinichloride*, $C_{60}H_{50}O_{12}N_2 \cdot H_2PtCl_6 \cdot 2\frac{1}{2}H_2O$, in the form of glistening needles which decompose at 182°. The *triacetate*, $C_5NH_4 \cdot C(CH_2 \cdot OAc)_3$, forms a thick oil, only sparingly soluble in water and of neutral reaction. The corresponding *platinichloride* melts at 159°.

When dimethylol-2-picoline is distilled in a current of steam, a volatile base, $C_5NH_4 \cdot CH \begin{smallmatrix} <CH_2> \\ <CH_2> \end{smallmatrix} O$, passes over. It is a colourless oil distilling at 130—134° under 11 mm. pressure, has an odour of tobacco juice, dissolves sparingly in water, and the solution has an alkaline reaction. The *hydrochloride* crystallises from alcohol and is extremely hygroscopic; the *mercurichloride*, $C_5H_9ON \cdot HCl \cdot 6HgCl_2$, forms glistening prisms, melts at 171—172°, and is very sparingly soluble in cold water; the *platinichloride* forms glistening, orange-red prisms, begins to decompose at 168°, and is readily soluble in hot water; the *aurichloride* crystallises in golden-yellow plates melting at 112·5—113·5°, and the *picrate* crystallises in yellow prisms melting at 109°. When boiled with hydrochloric acid, the anhydro-base is decomposed according to the equation

$$C_5NH_4 \cdot CH : C_2H_4O + H_2O = CH_2O + C_5NH_4 \cdot CH_2 \cdot CH_2 \cdot OH,$$

and monomethylol-2-picoline is formed. J. J. S.

5-Bromo-6-aminoquinoline. WILHELM MEIGEN (*J. pr. Chem.*, 1906, [ii], 73, 248—253. Compare this vol., i, 319).—The product obtained on brominating 6-aminoquinoline in glacial acetic acid is 5-bromo-6-aminoquinoline and not 7-bromo-6-aminoquinoline, as supposed by Claus and Schnell (*Abstr.*, 1896, i, 319), as it is obtained on reduction with iron and acetic acid of 5-bromo-6-nitroquinoline, which melts at 126° and is formed together with 5-bromo-8-nitroquinoline, melting at 146°, on nitration of 5-bromoquinoline.

5-Bromo-6-aminoquinoline crystallises in characteristic, silvery leaflets containing $2H_2O$, and melts at 83°, or, when anhydrous, at 127°. When diazotised and reduced with stannous chloride in hydrochloric acid solution, and the resulting tin salt boiled with sodium acetate and copper sulphate, 5-bromo-6-aminoquinoline yields a product which melts at 48° and is probably 5-bromoquinoline, containing small quantities of 5-chloroquinoline. On nitration, this yields a product melting at 136° which, when reduced, diazotised, and boiled with cuprous bromide, yields 5 : 8-dibromoquinoline.

5 : 6-Dibromoquinoline, obtained from 5-bromo-6-aminoquinoline, melts at 80—81°; it is formed also from 6-bromoquinoline by nitration and reduction and boiling the product with cuprous bromide. It forms a crystalline *platinichloride*; the *methiodide* crystallises in slender, yellow needles and melts at 250°.

5 : 6-Dibromo-8-nitroquinoline, formed from 5 : 6-dibromoquinoline, crystallises in yellow needles and melts at 196°.

The constitution of Claus' dibromoquinoline, melting at 135° (*Abstr.*, 1896, i, 254), remains to be determined. G. Y.

3-Phenylcinchonic Acid. H. HÜBNER (*Ber.*, 1906, **39**, 983—985).—*Potassium 3-phenylcinchonate* is prepared by heating 2 mols. of isatin and 1 mol. of phenylacetaldoxime in an excess of concentrated aqueous potassium hydroxide on the water-bath for twelve hours. The acid, $C_6H_4 \begin{smallmatrix} \diagup C(CO_2H):CPh \\ \diagdown N \quad \quad \quad CH \end{smallmatrix}$, crystallises in microscopic cubes or short prisms, melts at 273° , is sparingly soluble in glacial acetic acid or acetone, and is almost insoluble in other organic solvents. The *sodium* salt forms glistening crystals; the *silver* salt, $C_{16}H_{10}O_2NaAg$, was analysed; the *sulphate* forms long, transparent needles; the *chromate*, $(C_{16}H_{11}O_2N)_2CrO_3$, is obtained as a dark yellow powder. When treated with thionyl chloride, the acid forms a sparingly soluble, crystalline product, which is probably the *hydrochloride* of the acid chloride; this reacts with methyl alcohol, ammonia, aniline, or hydrazine to form the following substances: the *methyl ester*, $C_9NH_5Ph \cdot CO_2Me$, crystallises in white needles and melts at 73° ; the *amide*, $C_9NH_5Ph \cdot CO \cdot NH_2$, forms a microcrystalline powder and melts at 274° ; the *anilide*, $C_{22}H_{16}ON_2$, crystallises in needles and melts at 222° ; the *hydrazide*, $C_{16}H_{13}ON_3 \cdot H_2O$, crystallises in long, hexagonal plates and melts at 154° . G. Y.

Derivatives of 5-Phenylacridine. I. ALBERT E. DUNSTAN and ROBERT O'F. OAKLEY (*Ber.*, 1906, **39**, 977—980).—The *chromate* of 5-phenylacridine (Bernthsen, *Abstr.*, 1883, 580), $(C_{19}H_{13}N)_2H_2CrO_4$, forms a voluminous, yellow precipitate.

2:8-Diamino-5-phenylacridine, $C_{19}H_{15}N_3$, obtained by reducing 2:8-dinitro-5-phenylacridine (Bernthsen, *Ber.*, 1884, 1356) with stannous chloride in alcoholic hydrochloric acid, crystallises in nodular aggregates, and is darker coloured than chrysaniline. The *picrate*, $C_{19}H_{15}N_3(C_6H_3O_7N_3)_3$, the *platinichloride*, $C_{19}H_{15}N_3 \cdot H_2PtCl_6$, and the *dichromate*, $(C_{19}H_{15}N_3)_2 \cdot H_2Cr_2O_7$, were analysed; the *diacetyl* derivative is orange-yellow, and forms a *methiodide* which dissolves in methyl alcohol to a red solution. G. Y.

Derivatives of 5-Phenylacridine. II. Halogen Derivatives of the Acridine Group. ALBERT E. DUNSTAN and ROBERT O'F. OAKLEY (*Ber.*, 1906, **39**, 981—982).—Bromination of 5-phenylacridine leads to the formation of a *monobromo*-derivative, $C_{19}H_{12}NBr$, which crystallises in yellow needles, has no constant melting point, and does not form fluorescent solutions; with an excess of bromine in presence of iodine, a *tribromo*-derivative, $C_{19}H_{10}NBr_3$, crystallising in brown needles, is formed.

The action of chlorine on 5-phenylacridine in chloroform solution leads to the formation of a fluorescent, yellow solution which slowly deposits the *dichloro*-derivative, $C_{19}H_{11}NCl_2$, in needles; this is obtained also as a yellow, voluminous precipitate when 5-phenylacridine is chlorinated with bleaching powder. G. Y.

Products of the Condensation of Rhodanic Acid with Aldehydes. GUIDO BARGELLINI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 35—43. Compare Zipser, *Abstr.*, 1903, i, 273, and Andreasch and Zipser, *Abstr.*, 1903, i, 855).—The condensation products described

by the author were prepared by heating rhodanic acid and an aldehyde in alcoholic solution with sulphuric or hydrochloric acid.

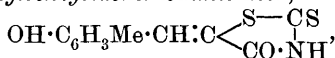
The salicylidene compound melts and decomposes at 218—219°; Zipser (*loc. cit.*) gave 200° as the melting point.

m-Hydroxybenzylidenerrhodanic acid, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{C} \begin{smallmatrix} \text{S}-\text{CS} \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$, crys-

tallises from aqueous alcohol in greenish-yellow needles melting at 244—245° and dissolves readily in alcohol, acetic acid, ethyl acetate, or acetone, and to a slight extent in benzene or chloroform.

p-Hydroxybenzylidenerrhodanic acid, $\text{C}_{10}\text{H}_7\text{O}_2\text{NS}_2$, crystallises from aqueous alcohol in reddish-yellow needles which begin to melt and decompose at 260° and dissolves readily in ethyl or amyl alcohol, acetic acid, ethyl acetate, ether, or acetone, and to a less extent in benzene or chloroform.

2-Hydroxy-5-methylbenzylidenerrhodanic acid,



prepared from rhodanic acid and *p*-homosalicylaldehyde, crystallises from aqueous alcohol in litharge-yellow needles melting and decomposing at 217—218°, and dissolves readily in alcohol, acetic acid, ethyl acetate, ether, or acetone, and moderately so in benzene or chloroform.

4-Hydroxy-3-methoxybenzylidenerrhodanic acid, $\text{C}_{11}\text{H}_9\text{O}_3\text{NS}_2$, prepared from rhodanic acid and vanillin, crystallises from acetic acid in lemon-yellow needles melting at 227—230°, and dissolves moderately well in alcohol, ethyl acetate, or acetone, and sparingly in ether, benzene, or chloroform.

3:4-Methylenedioxybenzylidenerrhodanic acid begins to turn brown at 256°, and at 258° is converted into a semi-fused, black mass (compare Andreasch and Zipser, *loc. cit.*).

Cinnamylidenerrhodanic acid melts at 220—221°; according to Zipser (*loc. cit.*), it melts and decomposes at 208—211°. By the action of bromine in chloroform solution it is converted into a yellowish-white compound melting and decomposing at about 160°.

Furfurylidenerhodanic acid, $\begin{smallmatrix} \text{CH}-\text{O} \\ || \\ \text{CH}\cdot\text{CH} \end{smallmatrix} \geq \text{C}\cdot\text{CH}\cdot\text{C} \begin{smallmatrix} \text{S}-\text{CS} \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$, crystallises

from alcohol in yellowish-orange needles, commencing to melt and decompose at 220°, and completely changing to a black liquid at 230°; it dissolves readily in acetic acid, acetone, ether, or chloroform, and sparingly in benzene. T. H. P.

Action of Grignard's Reagents on Michler's Ketone. MARTIN FREUND and FRITZ MAYER (*Ber.*, 1906, 39, 1117—1119. Compare Klages, *Abstr.*, 1902, i, 666).—The action of magnesium methyl iodide on Michler's ketone leads to the formation of *tetramethyldiaminodiphenylethylene*, $\text{CH}_2\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, which crystallises in glistening leaflets, melts at 115—117°, and is reduced by red phosphorus and hydriodic acid to tetramethyldiaminodiphenylethane. *Tetramethyldiaminodiphenylpropylene*, $\text{CHMe}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, forms small, greenish-yellow needles, melts at 99—100°, and is reduced to *tetramethyldiamino-*

diphenylpropane, $\text{CH}_2\text{Me}\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, which crystallises in white needles and melts at $50-51^\circ$. C. S.

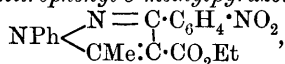
Action of Secondary Asymmetric Hydrazines on Sugar. III. RUDOLF OFNER (*Monatsh.*, 1906, 27, 75—80. Compare Abstr., 1905, i, 158, 937).—The *osazone*, $\text{C}_{22}\text{H}_{30}\text{O}_4\text{N}_4$, is formed in a few minutes by the action of *as*-phenylethyldiazine on lævulose in alcohol acetic acid solution, or is obtained in a yield of 55—60 per cent. of the theoretical when dextrose is digested with the hydrazine in alcohol acetic acid solution in a closed vessel for twenty hours at the laboratory temperature; it crystallises from ethyl acetate in slender, lemon-yellow needles and melts at 143° .

The *phenylethyldiazine*, $\text{C}_{14}\text{H}_{22}\text{O}_5\text{N}_2$, formed by the action of *as*-phenylethyldiazine on dextrose in boiling alcoholic solution, crystallises from ethyl alcohol in slender, white needles, which contain $\text{C}_2\text{H}_6\text{O}$, sinter at 80° , and melt at $116-118^\circ$, or from methyl alcohol in small plates which contain $\frac{1}{2}\text{CH}_4\text{O}$ and melt at $112-116^\circ$.

G. Y.

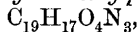
Pyrazole Derivatives. GAETANO MINUNNI and GUIDO LAZZARINI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 19—24. Compare Abstr., this vol., i, 114).—Ethyl 1:3-diphenyl-5-methylpyrazole-4-carboxylate, already obtained by Knorr and Blank (Abstr., 1885, 810), may be more readily prepared by the action of ethyl acetoacetate on benzaldehydephenylhydrazone.

Ethyl 1-phenyl-3-m-nitrophenyl-5-methylpyrazole-4-carboxylate,



prepared by the condensation of *m*-nitrobenzaldehydephenylhydrazone with ethyl acetoacetate in presence of zinc chloride, crystallises from alcohol in slender, colourless needles melting at $105.5-106.5^\circ$ and is sparingly soluble in light petroleum, more readily in ether or amyl alcohol, and very readily in benzene, ethyl acetate, or chloroform. The free acid, $\text{C}_{17}\text{H}_{13}\text{O}_4\text{N}_3$, crystallises from benzene with $\frac{1}{3}\text{C}_6\text{H}_6$ in rosettes of slender, white needles melting and decomposing at $207-208^\circ$ and dissolves in alcohol or chloroform and, to a slight extent, in ether.

Ethyl 1-phenyl-3-p-nitrophenyl-5-methylpyrazole-4-carboxylate,



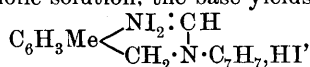
prepared from *p*-nitrobenzaldehydephenylhydrazone and ethyl acetoacetate, crystallises from alcohol in small, yellow needles melting at $107-108^\circ$ and dissolves sparingly in ether and readily in acetone or chloroform. The corresponding acid, $\text{C}_{17}\text{H}_{13}\text{O}_4\text{N}_3$, crystallises from benzene with $\frac{1}{3}\text{C}_6\text{H}_6$ in tufts of slender, white needles melting and decomposing at $209.5-210^\circ$ and dissolves slightly in ether and readily in alcohol or acetone. T. H. P.

Quinazolines from *o*-Amino-*m*-xylyl-*p*-toluidine. REINHOLD von WALTHER and R. BAMBERG (*J. pr. Chem.*, 1906, [ii], 73, 209—228. Compare Abstr., 1905, i, 298).—3-*p*-Tolyl-6-methyl-3:4-dihydroquinazo-

line, $\text{C}_6\text{H}_3\text{Me} \begin{array}{l} \text{N} = \text{CH} \\ \text{CH}_2 \cdot \text{N} \cdot \text{C}_7\text{H}_7 \end{array}$, is obtained by boiling *o*-amino-*m*-xylyl-

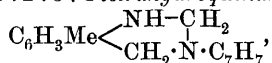
p-toluidine with ethyl *o*-formate, or with 80 per cent. formic acid, in a reflux apparatus; it crystallises in white, hexagonal leaflets, melts at 158°, and is readily soluble in benzene, chloroform, alcohol, or ether. The *hydrochloride*, $C_{16}H_{16}N_2 \cdot HCl \cdot 3H_2O$, crystallises in white needles, loses $3H_2O$ at 130°, and, when anhydrous, melts at 212°; the *nitrate* crystallises in long, slightly yellow needles, melts at 95°, and is decomposed at 170°; the *picrate*, $C_{22}H_{19}O_7N_5$, forms orange-yellow needles and melts at 201°; the *platinichloride*, $(C_{16}H_{16}N_2)_2 \cdot H_2PtCl_6$, crystallises in sheaves of yellow needles and melts at 202°.

With bromine in absolute alcoholic solution, the base forms the *additive* compound, $C_6H_3Me \left\langle \begin{array}{c} NBr_2 \cdot CH \\ | \\ CH_2 - N \cdot C_7H_7 \end{array} \right.$, which crystallises in red needles, and from which the base is re-formed on successive treatment with sulphur dioxide and potassium hydroxide in alcoholic solution. With iodine in alcoholic solution, the base yields the *product*



which forms red crystals having a metallic lustre, and decomposed by sulphur dioxide in alcoholic solution.

3-p-Tolyl-6-methyl-1:2:3:4-tetrahydroquinazoline,



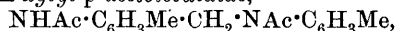
is prepared by reducing the dihydro-base with absolute alcohol and sodium; it crystallises in white needles, melts at 138°, and is readily soluble in benzene or chloroform, but only moderately so in alcohol or ether. The *hydrochloride* crystallises in white cubes, the *nitrate* in long, yellow needles, and the *sulphate* in small, white needles; the *platinichloride*, $(C_{16}H_{18}N_2)_2 \cdot H_2PtCl_6$, separates from glacial acetic acid in stout, yellow needles, or from alcohol in microscopic, brown crystals, and melts at 203–205°; the *picrate*, $C_{22}H_{21}O_7N_5$, crystallises in orange-yellow needles, becomes red on exposure to air, and melts at 200°.

The action of methyl iodide and methyl alcohol on the tetrahydro-base in a sealed tube at 100° leads to the formation of *3-p-tolyl-1:6-*

dimethyl-1:2:3:4-tetrahydroquinazoline, $C_6H_3Me \left\langle \begin{array}{c} NMe \cdot CH_2 \\ | \\ CH_2 - N \cdot C_7H_7 \end{array} \right.$,

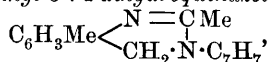
which crystallises in rhombic plates and melts at 155°. The *hydrochloride* forms quadratic plates, and the *platinichloride* sheaves of crystals.

o-Acetyl-amino-m-xylyl-p-acetotoluidide,



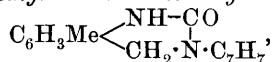
formed by heating *o*-amino-*m*-xylyl-*p*-toluidine with acetic anhydride on the water-bath, crystallises in hexagonal leaflets, melts at 135°, and when boiled with dilute hydrochloric or sulphuric acid, or heated with dilute hydrochloric acid under pressure at 160°, is hydrolysed with formation of the base.

3-p-Tolyl-2:6-dimethyl-3:4-dihydroquinazoline,



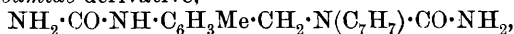
is formed when *o*-amino-*m*-xylyl-*p*-toluidine is heated with acetimino-ether in benzene solution; it crystallises from light petroleum in nodular aggregates of large, stout crystals and melts at 89—93°. The *hydrochloride* crystallises in transparent, quadratic leaflets and melts at 261°; the *platinichloride* forms sheaves of orange-yellow needles melting at 235°, or quadratic leaflets melting and decomposing at 207°.

2-Keto-3-p-tolyl-6-methyl-1 : 2 : 3 : 4-tetrahydroquinazoline,



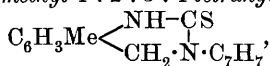
is obtained (1) by heating *o*-amino-*m*-xylyl-*p*-toluidine with carbamide at about 150°, or (2) by passing carbonyl chloride into a solution of the *p*-toluidine derivative in benzene; it crystallises in white needles, melts at 238—240°, and is readily soluble in hot alcohol, ethyl acetate, or benzene.

The *dicarbamide* derivative,



formed by the action of potassium cyanate on *o*-amino-*m*-xylyl-*p*-toluidine in hydrochloric acid solution, is obtained as a white, crystalline powder and melts and decomposes forming the keto-tetrahydroquinazoline at 219°.

2-Thion-3-p-tolyl-6-methyl-1 : 2 : 3 : 4-tetrahydroquinazoline,



prepared by heating *o*-amino-*m*-xylyl-*p*-toluidine with carbon disulphide and flowers of sulphur in absolute alcohol in a sealed tube at 130—160°, is obtained in a yield of 83 per cent. of the theoretical; it crystallises in transparent, hexagonal leaflets, becomes yellow at 200°, melts at 258—260°, and forms sparingly soluble salts. When reduced with sodium and alcohol, it yields the tetrahydro-base melting at 138°. The *sulphate* forms small, twisted needles and does not melt at 275°; the *hydrochloride* crystallises in leaflets and melts at 220—225°; the *platinichloride* forms microscopic, orange-yellow crystals, and melts and decomposes at 250°; the *picrate* forms transparent, hexagonal, yellow plates and melts at 240°; the *acetate* crystallises in hexagonal plates and melts at 257°; the *oxalate* crystallises in long, white needles and melts at 247—252°.

When heated with methyl iodide and methyl alcohol in a sealed tube at 130°, the thiontetrahydroquinazoline yields the *additive*

compound, $\text{C}_6\text{H}_3\text{Me} \begin{array}{l} \text{NH-CS} \cdot \text{MeI} \\ \text{CH}_2 \cdot \text{N} \cdot \text{C}_7\text{H}_7 \end{array}$, which crystallises in yellow prisms,

commences to become brown at 255°, melts and decomposes at 260°, and when heated with 70 per cent. alcohol forms *2-methylthiol-3-p-*

tolyl-6-methyl-3 : 4-dihydroquinazoline, $\text{C}_6\text{H}_3\text{Me} \begin{array}{l} \text{N}=\text{C} \cdot \text{SMe} \\ \text{CH}_2 \cdot \text{N} \cdot \text{C}_7\text{H}_7 \end{array}$. This

crystallises in delicate, white leaflets, or small, transparent prisms and melts at 87°; the *sulphate* forms long, slender, white needles and melts at 208°; the *hydrochloride* forms short spears and melts at 258°; the *platinichloride* forms microscopic, stout crystals and melts at 222°; the *picrate* forms slender, yellow needles and melts at 168°. When

reduced with zinc dust and dilute sulphuric acid, the methylthiol base yields 3-*p*-tolyl-6-methyl-1:2:3:4-tetrahydroquinazoline, melting at 138°. G. Y.

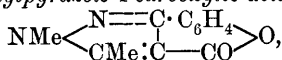
Action of Amyl Nitrite on Oximes. HARTWIG FRANZEN and F. ZIMMERMANN (*J. pr. Chem.*, 1906, [ii], 73, 253—256. Compare Minunni and Ciusa, this vol., i, 187).—The action of amyl nitrite on benzaldoxime in ethereal or benzene solution leads to the formation, (1) when cooled by ice, of benzaldoxime peroxide, which melts at 105°, together with benzaldehyde and benzoic acid, or, (2) when heated, of dibenzenzylazoxime, which melts at 108°.

The following substances are formed from the corresponding aldoximes in the same way.

m-Nitrobenzaldoxime peroxide melts at 124°; di-*m*-nitrobenzenylazoxime melts at 184°; di-*m*-chlorobenzenylazoxime, $\text{N} \begin{smallmatrix} \text{C}(\text{C}_6\text{H}_4\text{Cl}) \cdot \text{N} \\ \text{C}(\text{C}_6\text{H}_4\text{Cl}) \cdot \text{O} \end{smallmatrix}$, separates from benzene as a white precipitate and melts at 115°; *p*-methoxybenzaldoxime peroxide, $\text{O}_2(\text{N}:\text{CH}:\text{C}_6\text{H}_4:\text{OMe})_2$, crystallises in glistening, brown leaflets and melts at 119.5°.

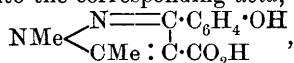
The action of ethyl nitrite on benzaldoxime and *p*-methoxybenzaldoxime in ethereal solution leads to the formation of benzaldoxime and *p*-methoxybenzaldoxime peroxides respectively. G. Y.

1-Phenyl-3-hydroxyphenyl-5-methylpyrazole-4-carboxylic Acid and its Lactone. GAETANO MINUNNI and G. LAZZARINI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 136—138).—The lactone of 1-phenyl-3-hydroxyphenyl-5-methylpyrazole-4-carboxylic acid,



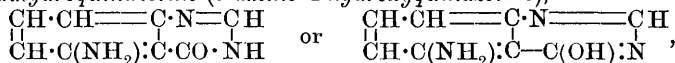
obtained by condensing *o*-hydroxybenzaldehydephenylhydrazone with ethyl acetoacetate in presence of zinc chloride, crystallises from alcohol in slender, white needles melting at 182—183° and dissolves sparingly in ether or benzene and readily in chloroform or acetone.

When heated with 10 per cent. potassium hydroxide solution, the lactone is converted into the corresponding acid,



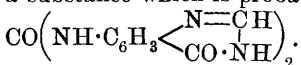
which crystallises from alcohol in slender, white needles melting and decomposing at about 160° and dissolves in benzene and very readily in chloroform, acetone, or ether. T. H. P.

5-Amino-4-ketodihydroquinazoline and 5-Amino-4-keto-2-methyldihydroquinazoline. MARSTON T. BOGERT and VICTOR J. CHAMBERS (*J. Amer. Chem. Soc.*, 1906, 28, 207—213).—5-Amino-4-ketodihydroquinazoline (5-amino-4-hydroxyquinazoline),

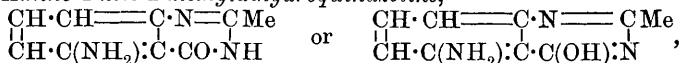


prepared by the action of stannous chloride on 5-nitro-4-ketodihydroquinazoline (Abstr., 1905, i, 613), crystallises in long, slender needles with 1H₂O, melts at 235—236° (corr.), and is soluble in water,

alcohol, acetone, or ethyl acetate; it dissolves in solutions of alkali hydroxides and is reprecipitated by carbon dioxide. The *hydrochloride* crystallises in needles; the *platinichloride* crystallises with $2\text{H}_2\text{O}$. The *dibromo-derivative*, obtained as a flocculent precipitate by adding bromine water to a warm aqueous solution of the quinazoline, gradually darkens on exposure to light. 5-Acetyl-amino-4-ketodihydroquinazoline forms colourless, slender needles, melts and darkens at $285\text{--}286^\circ$ (corr.), is soluble in warm acetone or alcohol, and yields a bromo-derivative. The corresponding *benzoyl derivative* crystallises in white, lustrous needles and melts at $263\text{--}264^\circ$ (corr.). 5-Phenyl-carbamido-4-ketodihydroquinazoline, obtained by the action of phenyl-carbimide on the aminoquinazoline, forms slender, white needles and is easily soluble in warm alcohol and slightly so in warm benzene; when heated, it melts at $250\text{--}260^\circ$ with formation of carbanilide and a substance which is probably the symmetrical *diquinazolylcarbamide*,



5-Amino-4-keto-2-methyldihydroquinazoline,



obtained by the reduction of 5-nitro-4-keto-2-methyldihydroquinazoline with stannous chloride, forms pale reddish-brown needles, melts and decomposes at $295\text{--}310^\circ$, slowly darkens on exposure to light, and is soluble in alcohol, acetone, or ethyl acetate; it dissolves in dilute alkali hydroxides and is reprecipitated by carbon dioxide or dilute acids. The *hydrochloride* and *platinichloride* were obtained as crystalline precipitates. E. G.

Thiazines. ROBERT GNEHM and FELIX KAÜFLER (*Ber.*, 1906, 39, 1016—1020. Compare *Abstr.*, 1904, i, 687, 935; Gnehm and Schröter, this vol., i, 211; Kehrmann, *Abstr.*, 1902, i, 566).—When heated with alcoholic ammonia in a sealed tube at $140\text{--}150^\circ$ for four hours, methylene-blue hydrochloride yields *as-dimethyl-leucothionine*, $\text{NMe}_2\cdot\text{C}_6\text{H}_3\left\langle\begin{array}{c}\text{NH} \\ \text{S}\end{array}\right\rangle\text{C}_6\text{H}_3\cdot\text{NH}_2$, which crystallises from light petroleum

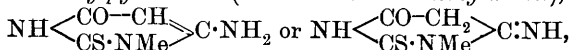
in green needles, melts at about 160° , is readily soluble in benzene or toluene, and is rapidly oxidised by air to *as-dimethylthionine*; this is identical with Formánek's dye (*Abstr.*, 1905, ii, 217). The *hydrochloride*, $\text{C}_{14}\text{H}_{14}\text{N}_3\text{S}\cdot\text{HCl}$, is obtained as a dark blue, crystalline mass, and is readily soluble in water, forming a blue solution which becomes red on addition of an alkali hydroxide, or in boiling methyl or ethyl alcohol, forming an intensely blue solution with a bluish-red fluorescence.

When heated with benzylamine in alcoholic solution at $130\text{--}140^\circ$ under pressure, methylene-blue forms *benzoylamino-tetramethylthionine*, which is isolated in the form of its *iodide*, $\text{C}_{23}\text{H}_{25}\text{N}_4\text{SI}$; this forms a violet powder with metallic lustre; the *hydrochloride* is readily soluble in water or alcohol, forming a blue solution, the absorption spectrum of which resembles that of methylene-blue; on addition of an alkali hydroxide to the aqueous solution, a reddish-violet precipitate is formed.

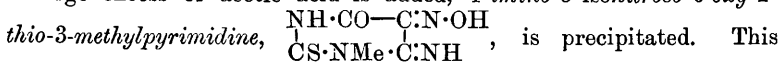
Successive treatment of dimethylthionine with sodium nitrite and potassium xanthate in hydrochloric acid solution leads to the formation of the *thioncarbonate* of thiazinemercaptan, which is obtained as a violet resin. When heated with 80 per cent. sulphuric acid on the water-bath, this evolves carbonyl sulphide and yields a bluish-black powder, which dissolves in sodium sulphite solution, forming the *leuco*-derivative; when warmed with this solution, washed, and exposed to the air, cotton-wool is dyed a dull blue. G. Y.

Methylene-green. ROBERT GNEHM and E. WALDER (*Ber.*, 1906, 39, 1020—1022).—Methylene-green (nitromethylene-blue) is formed by the action of sodium nitrite, nitrogen trioxide, nitric oxide, or amyl nitrite on methylene-blue in dilute sulphuric or nitric acid solution. The *nitrate*, $C_{16}H_{17}O_2N_4S \cdot NO_3$, and *hydrobromide*, $C_{16}H_{17}O_2N_4SBr \cdot 2H_2O$, were analysed. G. Y.

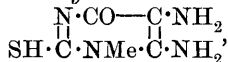
3-Methylhypoxanthine. WILHELM TRAUBE and FRIEDRICH WINTER (*Arch. Pharm.*, 1906, 244, 11—20).—Crystalline 4-*amino*-6-*oxy*-2-*thio*-3-*methylpyrimidine* (4-*amino*-2-*thio*-3-*methyluracil*),



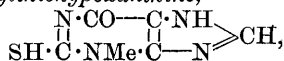
is obtained by boiling a solution of methylthiocarbamide in alcoholic sodium ethoxide with ethyl cyanoacetate. When a solution of it in normal aqueous sodium hydroxide is mixed with sodium nitrite and a large excess of acetic acid is added, 4-*imino*-5-*isonitroso*-6-*oxy*-2-*thio*-3-*methylpyrimidine*,



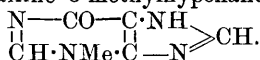
crystallises in violet-green needles; its salts are red, and the ammonium salt is but sparingly soluble. When this substance is added gradually to boiling aqueous yellow ammonium sulphide and the liquid filtered finally, yellow 4 : 5-*diamino*-6-*oxy*-2-*thiol*-3-*methylpyrimidine*,



crystallises out as the liquid cools. When this is boiled with formic acid, a yellow *formyl* derivative gradually separates, and when the *potassium* salt of this, $C_6H_5ON_4SK \cdot H_2O$ (obtained by dissolving the derivative in normal aqueous potassium hydroxide and precipitating with absolute alcohol), is heated at 250°, water is lost and crystalline 3-*methylthiohypoxanthine*,



is formed. When this is warmed with 25 per cent. nitric acid, it is oxidised to crystalline 3-*methylhypoxanthine*,



This substance dissolves in 210 parts of water, decomposes without melting when heated, forms well-crystallised salts with alkalis, dissolves readily in dilute mineral acids, and forms a crystalline

platinichloride. The position of the methyl group is known from the fact that the 4-amino-6-oxy-2-thiomethylpyrimidine, when subjected to prolonged heating with aqueous hydrogen peroxide, yields a product identified as 4-amino-2 : 6-dihydroxy-3-methylpyrimidine (Abstr., 1901, i, 54). C. F. B.

Coupling of Benzidine with Aniline. Diphenylbisdiazaminobenzene and Diphenylbisazoaminobenzene. LEO VIGNON (*Compt. rend.*, 1906, 142, 582—584).—When benzidine hydrochloride is diazotised and treated with aniline, dissolved in alcohol, in presence of sodium carbonate, or when diazobenzene chloride reacts with benzidine, (1) dissolved in cold alcohol in presence of sodium acetate, or (2) suspended in cold acetic acid, *diphenylbisdiazaminobenzene*,

$$\text{C}_{12}\text{H}_8(\text{N}_2\cdot\text{NHPh})_2,$$

is formed. This separates from benzene in yellowish-red crystals, melts at 180° , and is decomposed by 50 per cent. sulphuric acid, evolving much nitrogen. Its constitution was established by its hydrolysis into aniline and γ -dihydroxydiphenyl by boiling it with dilute sulphuric acid for fifteen minutes. When warmed with aniline and a small quantity of aniline hydrochloride, it is converted into *diphenylbisazoaminobenzene*, $\text{C}_{12}\text{H}_8(\text{NH}\cdot\text{N}_2\text{Ph})_2$, which separates from alcohol as a reddish-yellow substance and melts at 158 — 159° . T. A. H.

Estimation of the Sugar Group in Proteids. OTTO KRUMMACHER (*Zeit. Biol.*, 1906, 47, 612—627).—The views held regarding the origin of glycogen from proteid make it necessary to estimate the reducing substance in those proteids used as food in the experiments. Witte's peptone has been used in some of these experiments on rabbits. One hundred grams of dry Witte's peptone yielded 2.53 grams of reducing substance reckoned as glucosamine. Washed meat yielded 0.48 gram per cent. reckoned in the same way. The methods employed are described in full, and a large section of the paper is devoted to the study of the reducing power of glucosamine.

W. D. H.

Salts of Casein. JOHN H. LONG (*J. Amer. Chem. Soc.*, 1906, 28, 372—384).—The equivalent weights of the casein of cow's milk and of goat's milk have been determined by titration with $N/10$ alkali hydroxide in presence of phenolphthalein and have been found to be 1124 and 1190 respectively. The greater equivalent weight of the casein of goat's milk indicates the presence of a small additional complex in the molecule or of some small group not readily separated in the preparation of the casein.

The electrical conductivity has been measured of solutions of the normal acid and basic sodium salts, the normal potassium and ammonium salts, and the normal and acid lithium salts of the casein of cow's milk, and of the normal sodium and potassium salts of the casein of goat's milk, and it has been found that the conductivities of the two forms of casein for equal amounts of alkali are nearly the same.

The sodium salt of the casein of goat's milk has $[\alpha]_D - 105^\circ$ at 20° , which is slightly larger than that given by the corresponding salt of the casein of cow's milk (compare Abstr., 1905, ii, 498). E. G.

Method for the Study of Proteolytic and Gelatinolytic Enzymes. CLAUDIO FERMI (*Arch. Hygiene*, 1906, 55, 140—205).—The method described consists in estimating the exact numerical relationships of proteolytic ferment action by the method usually known as Mett's; the tubes are filled with gelatin, this being stated to be more sensitive than a number of other substances tried. In relation to trypsin action, the sensitiveness is increased by making the gelatin alkaline with sodium carbonate. The strength of the gelatin employed and certain other factors have also to be considered. The results are given in numerous tables. The paper contains a discussion on the question of priority in the use of the method, and also of the modification of gelatin plates sometimes employed. W. D. H.

Magnesium Compound of Organic Triphenylmethyl Chloride. Preparation of Triphenylmethane and Triphenylacetic Acid. JULIUS SCHMIDLIN (*Ber.*, 1906, 39, 628—636. Compare Sachs and Ehrlich, Abstr., 1904, i, 196; Gomberg and Cone, Abstr., 1905, i, 641; Baeyer, *ibid.*, 766.)—Magnesium reacts with triphenylmethyl chloride in presence of iodine, in ethereal solution in an atmosphere of hydrogen, to form the crystalline compound, $CPh_3 \cdot MgCl$, part of which remains dissolved as a yellow solution. The action of dry air on the magnesium compound in benzene solution leads to the formation of triphenylmethyl peroxide. When heated with dilute hydrochloric acid in an atmosphere of hydrogen in a reflux apparatus, the ethereal solution of the magnesium compound yields triphenylcarbinol, but the action of boiling hydrochloric acid on the solid magnesium compound, from which the ether has been distilled, leads to the formation of triphenylmethane, which is obtained in a yield of 78 per cent. of the triphenylmethyl chloride used. As triphenylmethyl chloride is prepared easily in good yields by Gomberg's method (Abstr., 1901, i, 77, 374), its conversion by means of its magnesium compound into triphenylmethane is the most advantageous method for the preparation of triphenylmethane.

Triphenylacetic acid is formed, together with small quantities of triphenylmethane, by the action of carbon dioxide on magnesium triphenylmethyl chloride in ethereal solution. The acid, which is obtained in a yield of 83 per cent. of the theoretical, crystallises from glacial acetic acid in long, glistening, white prisms and melts, decomposing to only a very slight extent, at $264\text{--}265^\circ$. G. Y.

Organic Chemistry.

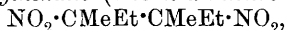
Symmetrical Tertiary α -Dinitroparaffins. IWAN I. BEWAD and A. PIRINSKY (*Ber.*, 1906, 39, 1231—1238).—The bromo-derivatives of secondary nitroparaffins react readily with finely-divided (molecular) silver, either with or without the addition of dry ether, yielding *s*-di-*tert*.-nitroparaffins, with the two nitro-groups attached to adjacent carbon atoms, $2\text{CBrRR}'\cdot\text{NO}_2 + 2\text{Ag} = 2\text{AgBr} + \text{NO}_2\cdot\text{CRR}'\cdot\text{CRR}'\cdot\text{NO}_2$.

A 65—70 per cent. yield of $\beta\gamma$ -dinitro- $\beta\gamma$ -dimethylbutane (*s*-*tert*.-dinitrohexane), $\text{NO}_2\cdot\text{CMe}_2\cdot\text{CMe}_2\cdot\text{NO}_2$, may be obtained from β -bromo- β -nitropropane. It crystallises from benzene in colourless, transparent plates or prisms, melts at $210\cdot5$ — $211\cdot5^\circ$, is insoluble in water or light petroleum, and dissolves sparingly in ether. When gently warmed, it sublimes; it appears to be identical with the compounds described by Zelinsky (*J. Russ. phys. chem. Ges.*, 1894, 26, 610) and by Konowaloff (*Abstr.*, 1895, i, 633). When reduced with tin and hydrochloric acid, it yields the corresponding diamine. The *hydrochloride*,



crystallises from dilute alcohol in colourless needles and decomposes at 310° . The *platinichloride*, $\text{C}_6\text{H}_{18}\text{N}_2\text{PtCl}_6\cdot 2\text{H}_2\text{O}$, crystallises in orange-yellow needles or plates and decomposes at 280° . The *aurichloride*, $\text{C}_6\text{H}_{16}\text{N}_2\cdot 2\text{HAuCl}_4\cdot 4\text{H}_2\text{O}$, forms large, transparent, yellow prisms or plates. The *base* melts at about 100° and distils at 147 — 149° under 740 mm. pressure. It is very volatile and also extremely hygroscopic, and dissolves with the greatest readiness in ether or water. Pinacolin is formed when an aqueous solution of the nitrite of the base is distilled.

$\gamma\delta$ -Dinitro- $\gamma\delta$ -dimethylhexane (*s*-*tert*.- α -dinitro-octane),



crystallises from ether in small, rectangular plates, melts at 79 — 80° , sublimes even at 40° , and dissolves readily in most organic solvents with the exception of light petroleum. The corresponding *diamine* yields a *hydrochloride* which begins to decompose at 270° , a *platinichloride*, $\text{C}_8\text{H}_{22}\text{N}_2\text{PtCl}_6\cdot 5\text{H}_2\text{O}$, and an *aurichloride*,



which, in the anhydrous form, melts and decomposes at 198 — 200° .

J. J. S.

Preparation of Aldehyde-free Alcohol for Use in Oil and Fat Analysis. FREDERICK L. DUNLOP (*J. Amer. Chem. Soc.*, 1906, 28, 395—398).—Mere treatment with potassium hydroxide and distillation does not lead to the desired result. The following process is therefore recommended.

To 1 litre of 95 per cent. alcohol are added 1·5 grams of silver nitrate dissolved in 3 c.c. of water. To this are then added very slowly 3 grams of potassium hydroxide dissolved in 15 c.c. of hot alcohol. Without shaking, the liquid is allowed to remain until the silver precipitate has completely settled, and the clear liquid is then submitted to distillation, when a perfectly neutral alcohol free from aldehyde is obtained.

L. DE K.

Action of Organo-magnesium Compounds on Crotonaldehyde. JEAN REIF (*Ber.*, 1906, 1603—1604).—Magnesium ethyl bromide and crotonaldehyde in ethereal solution yield a product from which Δ^{β} -hexene- δ -ol, $\text{CHMe}:\text{CH}:\text{CHEt}:\text{OH}$, is obtained on the addition of cold dilute sulphuric acid. The alcohol is a colourless, mobile liquid, and distils at $85\text{--}87^{\circ}$ under 120 mm. pressure, or at $133\text{--}134^{\circ}$ under atmospheric pressure. The acetate distils at $153\text{--}155^{\circ}$, the chloride, δ -chloro- Δ^{β} -hexene, $\text{C}_6\text{H}_{11}\text{Cl}$, at $122\text{--}126^{\circ}$, and δ methoxy- Δ^{β} -hexene, $\text{C}_7\text{H}_{14}\text{O}$, at $110\text{--}113^{\circ}$.

From magnesium propyl bromide, Δ^{β} -heptene- δ -ol, $\text{CHMe}:\text{CHPr}:\text{OH}$, is formed; it distils at $152\text{--}154^{\circ}$, or at $104\text{--}105^{\circ}$ under 120 mm. pressure. The acetate, $\text{C}_9\text{H}_{16}\text{O}_2$, distils at $168\text{--}170^{\circ}$. J. J. S.

Derivatives of Pyrophosphoric Acid. JACQUES CAVALIER (*Compt. rend.*, 1906, 142, 885—887. Compare Abstr., 1904, ii, 658).—Ethyl, *n*-propyl, isopropyl, *n*-butyl, amyl, and allyl pyrophosphates have been prepared by the action of silver pyrophosphate on the corresponding alkyl iodide. The esters are liquid at the ordinary temperature, decompose when heated, and cannot be distilled. They are soluble in benzene, carbon disulphide, carbon tetrachloride, and ether. Ethyl pyrophosphate is also soluble in water, but the solution has a strongly acid reaction, indicating either hydrolysis or formation of an orthophosphoric derivative. The cryoscopic determination of the molecular weights of the esters in benzene solution gave values corresponding with the formula $\text{R}_4\text{P}_2\text{O}_7$. In the case of the isopropyl and allyl esters, which were obviously impure, the molecular weight values were greater than those required by theory. H. M. D.

Composition of Petroleum. Sulphur Compounds and Unsaturated Hydrocarbons in Canadian Petroleum. CHARLES F. MABERY and WILLIAM O. QUAYLE (*Amer. Chem. J.*, 1906, 35, 404—432. Compare Mabery and Smith, Abstr., 1891, 1172).—A series of sulphur compounds has been isolated from Canadian petroleum by fractional distillation and subsequent treatment with alcoholic mercuric chloride. The mercuric chloride precipitates are obtained in the crystalline form from the lower fractions and as viscous or oily masses from the less volatile portions. The sulphur compounds are regenerated from the mercuric chloride precipitates by means of hydrogen sulphide and are further purified by fractional distillation. The substances are members of a new series for which the name "thiophan" is suggested. They combine with chloroplatinic acid with formation of heavy, viscous oils. When the thiophans are heated with ethyl iodide in a sealed tube, additive compounds, $\text{C}_n\text{H}_{2n}\text{S}, \text{EtI}$, are formed, which crystallise in small prisms and, when warmed with silver oxide and water, are converted into the corresponding hydroxides, which have an alkaline reaction. The thiophans combine violently with bromine with evolution of a quantity of hydrogen bromide equivalent to that of the bromine added, and are readily oxidised by potassium permanganate or chromic acid with formation of sulphones. In empirical composition, the thiophans correspond with hydrothiophens which have not hitherto

been synthesised, but their constitution has not yet been established. The following compounds have been isolated.

Heptylthiophan, $C_7H_{14}S$, boils at $74-76^\circ$ under 50 mm. or at $158-160^\circ$ under 750 mm. pressure, has a sp. gr. 0.8878 at 20° , and n_D 1.468.

Octylthiophan, $C_8H_{16}S$, boils at $81-83^\circ$ under 50 mm. or at $167-169^\circ$ under atmospheric pressure, has a sp. gr. 0.8929 at 20° , and n_D 1.4860.

isoOctylthiophan boils at $94-96^\circ$ under 50 mm. or at $183-185^\circ$ under atmospheric pressure, and has a sp. gr. 0.8937 at 20° .

Nonylthiophan, $C_9H_{18}S$, boils at $106-108^\circ$ under 50 mm. or at $193-195^\circ$ under atmospheric pressure, has a sp. gr. 0.8997 at 20° , and n_D 1.4746.

Decylthiophan, $C_{10}H_{20}S$, boils at $114-116^\circ$ under 50 mm. or at $207-209^\circ$ under 750 mm. pressure, has a sp. gr. 0.9074 at 20° , and n_D 1.4766.

Undecylthiophan, $C_{11}H_{22}S$, boils at $128-130^\circ$ under 50 mm. pressure, has a sp. gr. 0.9147 at 20° , and n_D 1.480.

Tetradecylthiophan, $C_{14}H_{28}S$, boils at $168-170^\circ$ under 50 mm. or at $266-268^\circ$ under 750 mm. pressure, has a sp. gr. 0.9208 at 20° , and n_D 1.4892.

Hexadecylthiophan, $C_{16}H_{32}S$, boils at $184-186^\circ$ under 50 mm. or at $283-285^\circ$ under 750 mm. pressure, has a sp. gr. 0.9222 and n_D 1.4903.

Octadecylthiophan, $C_{18}H_{36}S$, boils at $198-202^\circ$ under 50 mm. and at $290-295^\circ$ under atmospheric pressure, has a sp. gr. 0.9235 at 20° , and n_D 1.4977.

The following sulphones have been prepared. *Hexylthiophansulphone*, $C_6H_{12}SO_2$, is a thick, viscous oil, which has a sweet taste and odour. *Heptylthiophansulphone*, $C_7H_{14}SO_2$, is a thick, heavy oil, which has a sp. gr. 1.1138 at 20° . *Octylthiophansulphone*, $C_8H_{16}SO_2$, has a sp. gr. 1.1142 at 20° . *Nonylthiophansulphone*, $C_9H_{18}SO_2$, has a sp. gr. 1.1161 at 20° . *Undecylthiophansulphone*, $C_{11}H_{22}SO_2$, has a sweet, pleasant odour and a sp. gr. 1.1126 at 20° . *Dodecylthiophansulphone*, $C_{12}H_{24}SO_2$, obtained by the action of potassium permanganate on the distillate boiling at $142-144^\circ$ under 50 mm. pressure, has a sp. gr. 1.1372 at 20° .

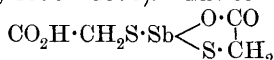
Canadian petroleum contains a small proportion of unsaturated hydrocarbons, probably of the ethylene series. These compounds were identified by converting them into the corresponding alkyl bromides by heating them with fuming hydrobromic acid. The fraction boiling at $70-80^\circ$ under atmospheric pressure yielded a *hexyl bromide* which boiled at $62-65^\circ$ under 50 mm. pressure. The fraction boiling at $98-102^\circ$ under atmospheric pressure furnished a *heptyl bromide* which boiled at $76-80^\circ$ under 50 mm. pressure and had a sp. gr. 1.1601. The fraction boiling at $118-119^\circ$ under atmospheric pressure gave an *octyl bromide* which boiled at $93-95^\circ$ under 50 mm. pressure and had a sp. gr. 1.1836. The fraction boiling at $140-141^\circ$ under atmospheric pressure yielded a *nonyl bromide* which boiled at $110-113^\circ$ under 50 mm. pressure and had a sp. gr. 1.2084.

Canadian petroleum also contains other hydrocarbons which differ

in odour and in other respects from those hitherto identified in petroleum, and are possibly terpenes. E. G.

Dehydration of β -Hydroxy- β -Alkylpivalic Esters. ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, [iii], 35, 217—223. Compare this vol., i, 230).—*Ethyl hydroxyethylpivalate* (ethyl β -hydroxy- α -dimethylvalerate), prepared by condensing propaldehyde with ethyl bromoisobutyrate, is a viscous liquid of pleasant odour and boils at 106° under 20 mm. pressure. The *acetyl* derivative boils at 127 — 128° under 37 mm. pressure. The free *acid*, $\text{OH}\cdot\text{CHEt}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$, crystallises from boiling ether, melts at 94° , and boils at 150 — 151° under 15 mm. pressure. The *calcium* and *copper* salts are crystalline. The *phenylcarbamate* crystallises from boiling water in long needles, melts at 100 — 101° , and is insoluble in benzene or light petroleum. When ethyl β -hydroxy- α -dimethylvalerate, dissolved in benzene, is treated with phosphoric oxide, it yields *ethyl α -dimethylpropenylacetate* [α -dimethyl- Δ^{β} -pentenoate], $\text{CHMe}\cdot\text{CH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$, and α -dimethylvalerolactone. The former is a colourless, mobile liquid of pleasant odour and boils at 162° . The free acid, identical with Perkin and Smith's crotonyldimethylacetic acid (*Trans.*, 1904, 85, 156), melts at -17° to a mobile liquid and boils at 119° under 24 mm. pressure. The *calcium*, *lead*, and *zinc* salts are crystalline. The *benzylamine* salt crystallises from ether and melts at 90° . The *amide* of the acid crystallises from a mixture of ether and light petroleum in silky spangles and melts at 88° , the *anilide* forms long needles from light petroleum and melts at 56° , the *phenylhydrazide* crystallises from ether and melts at 125 — 126° , and the *benzylamide*, obtained by heating molecular proportions of the acid and benzylamine at 180° for six hours, is a viscous liquid and boils at 190° under 20 mm. pressure. The *chloride* of the acid is a mobile liquid and boils at 56° under 21 mm. pressure. On reduction, dimethyl- Δ^{β} -pentenoic acid yields the corresponding $\beta\beta$ -dimethyl- Δ^{γ} -pentenol, $\text{CHMe}\cdot\text{CH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$, a liquid of pleasant odour boiling at 150° . The *acetyl* derivative boils at 167 — 168° . β -Bromo- α -dimethylvalerolactone, obtained by brominating dimethylhexenoic acid in chloroform, crystallises from ether, melts at 90° , and boils at 120° under 20 mm. pressure (compare Perkin and Smith, *loc. cit.*). T. A. H.

Antimony Derivatives of Thioglycollic Acid. LUDWIG RAMBERG (*Ber.*, 1906, 39, 1356—1358).—The compound



(compare Klason and Carlson, this vol., i, 232) is a moderately strong acid, but cannot be estimated volumetrically, as the end reaction is not sharp on account of partial hydrolysis of the internal ester. The *sodium*, *potassium*, and *barium* salts are described. The antimony cannot be estimated by electrolysis, but it is completely precipitated by hydrogen sulphide from a solution of the sodium salt. C. S.

Characteristic Reaction of Ethyl Glyoxylate. Action of Ammonia on the Ester and its Derivatives. LOUIS J. SIMON and G. CHAVANNE (*Compt. rend.*, 1906, 142, 930—933).—When ethyl

glyoxylate is heated with aqueous ammonia, a coloured substance with strong tinctorial properties is formed in accordance with the equation $2\text{COH}\cdot\text{CO}_2\text{Et} + 3\text{NH}_3 = 2\text{C}_2\text{H}_5\text{OH} + \text{C}_4\text{H}_9\text{O}_4\text{N}_3$. The substance is black in colour, slightly soluble in water, insoluble in alcohol; it dissolves in ammonia and in solutions of the alkali hydroxides and carbonates with a deep red coloration. The formation of a coloured substance appears to be quite characteristic of ethyl glyoxylate; it does not take place with the esters of acids closely related to glyoxylic nor with glyoxylic acid itself. The authors suggest that the coloured substance is the ammonium salt of the compound $\text{OH}\cdot\text{CH}\langle\begin{smallmatrix}\text{CO}\cdot\text{NH} \\ \text{NH}\cdot\text{CO}\end{smallmatrix}\rangle\text{CH}\cdot\text{OH}$, formed by condensation of two molecules of glyoxylamide. H. M. D.

Camphoric Acid. XV. Certain Derivatives of Aminolauronic Acid. WILLIAM A. NOYES and RENÉ DE M. TAVEAU (*Amer. Chem. J.*, 1906, 35, 379—386. Compare Abstr., 1904, i, 807).—When the nitroso-derivative of aminolauronic anhydride (1 mol.) is boiled with aqueous 10 per cent. sodium hydroxide (1.5 mols.), the following substances are produced: hydrocarbon, C_8H_{14} , 27.8 per cent.; isocampholactone, 21.4 per cent.; an unsaturated acid, $\text{C}_8\text{H}_{13}\cdot\text{CO}_2\text{H}$, 6.6 per cent.; liquid acids, probably consisting largely of γ -lauronic acid, 1.4 per cent.; hydroxylauronic acid, 1.7 per cent.; a new lactone, $\text{C}_8\text{H}_{14}\langle\begin{smallmatrix}\text{CO} \\ \text{O}\end{smallmatrix}\rangle$, 4.0 per cent.

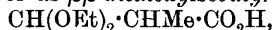
isocampholactone boils at 123.4° under 28 mm. and at 125.6° under 30 mm. pressure. The methyl ester of the corresponding hydroxy-acid, $\text{OMe}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}_2\text{H}$, obtained by the action of methyl iodide on the silver salt, boils at 150 — 153° under 19 mm. pressure, crystallises in needles, and melts at 84° .

The unsaturated acid, $\text{C}_8\text{H}_{13}\cdot\text{CO}_2\text{H}$, forms a white, curdy mass, boils, or rather sublimes, at 130 — 133° under 21 mm. pressure, melts at 152 — 154° , is readily oxidised by potassium permanganate, and is probably identical with the acid obtained by Walker and Henderson (*Trans.*, 1895, 37, 343) from the mixture of esters formed by the electrolysis of potassium *allo*-ethyl camphorate. The *silver* and *calcium* salts are described.

The new lactone, $\text{C}_8\text{H}_{14}\langle\begin{smallmatrix}\text{CO} \\ \text{O}\end{smallmatrix}\rangle$, boils at about 126° under 27 mm. pressure, forms beautiful crystals, melts at 164 — 165° , has $[\alpha]_D + 13.87^\circ$, and is insoluble in strong potassium carbonate solution. The corresponding hydroxy-acid, $\text{OH}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}_2\text{H}$, melts and decomposes at 189.5° ; its *barium* salt crystallises with $4\text{H}_2\text{O}$. E. G.

Capacity of Ethoxy-groups for Substitution by Radicles. Synthesis of Acetal-esters and of Homologous Ethyl Ethoxyacrylates. ALEXEI E. TSCHITSCHIBABIN (*J. pr. Chem.*, 1906, [ii], 73, 326—336. Compare Reformatsky, this vol., i, 136; Sokolowsky, *ibid.*, 138).—Sokolowsky's supposed triethyl *s*-trimethylbutanetricarboxylate, formed by the action of zinc and ethyl α -bromopropionate on ethyl orthoformate, is ethyl *as*- $\beta\beta$ -diethoxyisobutyrate, $\text{CH}(\text{OEt})_2\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$; when hydrolysed with 10 per cent. potassium

hydroxide and neutralised carefully with hydrochloric acid, it yields a viscid liquid consisting of *as*- $\beta\beta$ -diethoxyisobutyric acid,



together with a small quantity of Sokolowsky's acid melting at 109° , which is β -ethoxy- α -methylacrylic acid. When distilled, the acetal acid decomposes, leaving a small residue of β -ethoxy- α -methylacrylic acid, and yielding carbon dioxide and *ethyl propenyl ether*, $\text{CHMe}:\text{CH} \cdot \text{OEt}$, which boils at 68 — 72° , and forms an *additive* compound with bromine, and *aa*-diethoxypropane, boiling at 122° . Ethyl propenyl ether and *aa*-diethoxypropane are hydrolysed readily by acids, forming propaldehyde and alcohol. The acetal-acid, which yields propaldehyde when distilled when dilute sulphuric acid, forms soluble uncrystallisable salts, of which those of the heavy metals are unstable in aqueous solution.

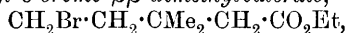
β -Ethoxy- α -methylacrylic acid, $\text{OEt} \cdot \text{CH}:\text{CH} \cdot \text{CMe} \cdot \text{CO}_2\text{H}$, is formed, together with small amounts of ethyl formylpropionate, by the action of cold dilute hydrochloric acid on ethyl *as*- $\beta\beta$ -diethoxyisobutyrate; it crystallises from light petroleum in large prisms, is hydrolysed by mineral acids, forming propaldehyde, alcohol, and carbon dioxide, and when boiled decomposes slowly into ethyl propenyl ether and carbon dioxide. The *ethyl* ester, formed by boiling the silver salt with ethyl iodide, boils at 200 — 201° , has the sp. gr. 0.9753 at $20^\circ/0^\circ$, and has an odour differing from that of the acetal-ester.

The action of zinc and ethyl bromoacetate on ethyl orthoformate leads to the formation of β -ethoxyacrylic acid, $\text{OEt} \cdot \text{CH}:\text{CH} \cdot \text{CO}_2\text{H}$, which crystallises in colourless prisms, melts at 110.5° , and is identical with Otto's ethoxyacrylic acid (Abstr., 1890, 957; compare Claisen, Abstr., 1898, i, 421). It is hydrolysed readily by mineral acids, forming acetaldehyde, alcohol, and carbon dioxide; the *silver* salt, $\text{C}_5\text{H}_7\text{O}_3\text{Ag}$, is obtained as a white powder; the *ethyl* ester, $\text{OEt} \cdot \text{CH}:\text{CH} \cdot \text{CO}_2\text{Et}$, boils at 195 — 196° and has the sp. gr. 0.9983 at $20^\circ/0^\circ$ or 1.0174 at $0^\circ/0^\circ$. G. Y.

Anhydrides of Diethylmalonic Acid. ALFRED EINHORN and HEINRICH VON DIESBACH (*Ber.*, 1906, **39**, 1222—1223).—A duodecimolecular *diethylmalonic anhydride*, $(\text{CEt}_2 \langle \text{CO} \rangle \text{O})_{12}$, is formed when diethylmalonyl chloride is treated with a dilute aqueous solution of pyridine; it is obtained as a slightly yellow, amorphous powder, melts at 80 — 85° , and decomposes when heated above its melting point. It dissolves in dilute potassium hydroxide, and is converted by ammonia into diethylmalonic acid, diethylmalonamide, and *diethylmalonamic acid*, $\text{NH}_2 \cdot \text{CO} \cdot \text{CEt}_2 \cdot \text{CO}_2\text{H}$, which crystallises in glistening, white, tetragonal plates, melts at 146° , forming carbon dioxide and diethylacetamide. The action of diethylamine on the anhydride at the ordinary temperature leads to the formation of diethylmalonic acid, *diethylmalondidiethylamic acid*, $\text{NEt}_2 \cdot \text{CO} \cdot \text{CEt}_2 \cdot \text{CO}_2\text{H}$, which crystallises in long prisms and melts at 88 — 90° , and *diethylacetyldiethylamide*, which is obtained as a colourless oil. This, which is the main product when the reacting mixture is not cooled, has an odour of menthol and boils at 108° under 12 mm. pressure.

If the amorphous anhydride is boiled in an indifferent solvent it is decomposed, forming carbon dioxide, α -ethylbutyric anhydride boiling at 226—229°, and the *quadrimeric anhydride* of diethylmalonic acid, $(\text{CEt}_2 \cdot \text{C} \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{CO} \end{smallmatrix} \text{O})_4$, which crystallises from ethyl acetate in rhombic plates, melts and decomposes at 220°, and behaves towards alkali hydroxides, ammonia, and diethylamine in the same way as the amorphous anhydride. G. Y.

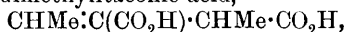
Synthesis of $\beta\beta$ -Dimethyl- and $\beta\beta\epsilon$ -Trimethyl-pimelic Acids. GUSTAVE BLANC (*Compt. rend.*, 1906, 142, 996—999).— $\beta\beta$ -Dimethyl-valerolactone, obtained by reducing $\beta\beta$ -dimethylglutaric anhydride (Abstr., 1905, i, 681), reacts with phosphorus pentabromide and alcohol to form *ethyl δ -bromo- $\beta\beta$ -dimethylvalerate*,



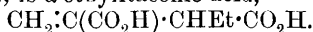
which is a colourless oil boiling at 119° under 10 mm. pressure; the corresponding *acid* crystallises from ether in large prisms melting at 58°. Ethyl δ -bromo- $\beta\beta$ -dimethylvalerate condenses readily with ethyl sodiomalonate when heated under pressure at 100° to form the corresponding *tricarboxylic ester*, $\text{CH}(\text{CO}_2\text{Et})_2 \cdot (\text{CH}_2)_2 \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, which boils at 180° under 7 mm. pressure and yields $\beta\beta$ -dimethyl-pimelic acid on heating with hydrochloric acid (compare Léser, Abstr., 1899, i, 743).

Ethyl δ -bromo- $\beta\beta$ -dimethylvalerate condenses with ethyl sodiomethylmalonate to form the corresponding *tricarboxylic ester*, which boils at 180—182° under 7 mm. pressure; the corresponding *acid*, $\text{CMe}(\text{CO}_2\text{H})_2 \cdot [\text{CH}_2]_2 \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, melts at 163°, and on heating at 180° is converted quantitatively into $\beta\beta\epsilon$ -trimethylpimelic acid melting at 55—56°. M. A. W.

$\alpha\gamma$ -Dimethyl- and α -Ethyl-itaconic Acids. FRITZ FICHTER and CARL SCHLAEFFER (*Ber.*, 1906, 39, 1535—1536).—Both acids formed by boiling methylethylmaleic anhydride with sodium hydroxide (Fichter and Rudin, Abstr., 1904, i, 473) yield anhydrides when treated with acetyl chloride, and must belong to the itaconic acid series. The acid melting at 202°, and termed previously methylethyl-fumaric acid, is $\alpha\gamma$ -dimethylitaconic acid,



as it is formed also by the action of sodium ethoxide on $\alpha\gamma$ -dimethylparaconic acid. The acid melting at 150°, and previously termed $\alpha\gamma$ -dimethylitaconic acid, is α -ethylitaconic acid,



$\alpha\gamma$ -Dimethylitaconic anhydride, $\text{CHMe} \cdot \text{C} \begin{smallmatrix} \diagup \text{CHMe} \cdot \text{CO} \\ \diagdown \text{CO} \end{smallmatrix} \text{O}$, is a colourless oil which boils at 131° under 16 mm. pressure, and when boiled with water yields the acid melting at 202°.

α -Ethylitaconic anhydride, $\text{CH}_2 \cdot \text{C} \begin{smallmatrix} \diagup \text{CHEt} \cdot \text{CO} \\ \diagdown \text{CO} \end{smallmatrix} \text{O}$, crystallises from light petroleum, melts at 52°, and when boiled with water is hydrolysed to the acid melting at 150°. G. Y.

Conversion of Cholic Acid into Cholamine. THEODOR CURTIUS (*Ber.*, 1906, 39, 1389—1391).—The *carbamate*, $C_{23}H_{39}O_3 \cdot NH \cdot CO_2Et$, is obtained when cholazide, $C_{23}H_{39}O_3 \cdot CON_3$, is boiled with absolute alcohol; it crystallises from ethyl acetate in small, doubly-refracting prisms, sinters at 125° , and melts and decomposes at 150° . By distillation in a vacuum with lime, it yields *cholamine*, $C_{23}H_{39}O_3 \cdot NH_2$, which separates from ethyl acetate in small, doubly-refracting, yellow needles; the aqueous solution is distinctly alkaline and has a bitter taste. The *hydrochloride*, $C_{23}H_{41}O_3N \cdot HCl$, is an amorphous, yellow powder which becomes brown at 80° , melts at 120° , and decomposes at 140° . The *platinichloride*, $(C_{23}H_{41}O_3N)_2 \cdot H_2PtCl_6$, is a yellow powder which becomes brown at 180° and melts at 193° to a dark brown liquid.

From the amine, an aldehyde, $C_{22}H_{37}O_2 \cdot CHO$, cannot be obtained by the elimination of ammonia, proving that the carboxyl group in cholic acid is not attached to $CH(OH)$. C. S.

New Method for the Preparation of Ketones. HUGO HAEHN (*Ber.*, 1906, 39, 1702—1705).—When dry fatty acids are passed through a tube packed with calcium carbide and warmed in a furnace, ketones are produced: $2R \cdot CO_2H = COR_2 + CO_2 + H_2O$. Formic acid yields carbon monoxide and water; acetic acid, a mixture of acetone and methyl alcohol; propionic acid gives diethyl ketone, and butyric acid, dipropyl ketone in 30 per cent. yield. *iso*Valeric acid gives valerone and small quantities of valeraldehyde. Benzoic acid and calcium carbide react at a low red heat, best under 20 mm. pressure, with the formation of benzophenone. C. S.

Stable Compounds of Hyposulphites with Ketones. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 162875).—Solutions of hyposulphites are rendered more stable by addition of acetone, and this method has been employed to preserve them. It is now found that solid compounds of hyposulphites with acetone or methyl ethyl ketone are formed in the presence of alkalis, preferably sodium hydroxide and ammonia. The products obtained on evaporating the solution resist a temperature of 50° without deterioration. Those obtained in the absence of ammonia are less stable. Solutions of the ketone compounds only reduce indigotin slowly in the cold, more rapidly on warming. C. H. D.

Syntheses with *d*-Gluconic Acid. CARL PAAL and FRANZ HÖRNSTEIN (*Ber.*, 1906, 39, 1361—1364).—With the object of adding hydrocarbon residues to the carbon chain of pentoses and hexoses by the action of Grignard's reagents on the corresponding lactones (compare Houben, *Abstr.*, 1904, i, 334), the authors have prepared, by heating *d*-gluconic acid (1 mol.) and acetic anhydride (4 mols.) on the water-bath, a gum which they regard as a mixture of tetra-acetyl-*d*-gluconolactone and triacetyl-*d*-gluconolactone-ethylglucoside, having in alcoholic solution, after twenty-four hours, $[\alpha]_D 50.9^\circ$. The action on this mixture of an excess (12 mols.) of magnesium phenyl bromide, in ether-benzene solution, leads to the formation of diphenylmethyl-

carbinol and $\alpha\beta\gamma\delta\epsilon\zeta$ -hexahydroxy- $\alpha\alpha$ -diphenylhexane ($\alpha\alpha$ -diphenyl-d-sorbitol?), $\text{OH}\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{OH}]_4\cdot\text{CPh}_2\cdot\text{OH}$. The two compounds are separated, after removal of the ether and benzene, by solution of the former in light petroleum; the residual grey mass, after repeated crystallisation from ethyl acetate or absolute alcohol, is obtained in white needles. The substance melts at $154\text{--}157^\circ$ and in alcoholic solution has $[\alpha]_D$ 77.9° . C. S.

Condensation of Formaldehyde. OSCAR LOEW (*Ber.*, 1906, 39, 1592—1593. Compare *Abstr.*, 1888, 358; 1889, 581; Euler and Euler, this vol., i, 142).—A claim for priority. G. Y.

Part played by Formaldehyde in the Caramelisation of Sugar. AUGUSTE TRILLAT (*Chem. Centr.*, 1906, i, 978; from *Bull. Assoc. Chim. Sucr. Dist.*, 23, 652—655. Compare this vol., i, 234, 235).—A portion of the formaldehyde which is formed when sugar is heated polymerises and forms products which are analogous to methylenitan or formose, and the caramel itself may possibly be formed from these polymerides. This hypothesis is supported by the fact that when solutions of formaldehyde are treated with small quantities of alkali or metallic oxide at higher temperatures, a brown, amorphous substance is formed which has the same taste and odour, and apparently all the properties of the caramel which is obtained from sugar. When 100 parts of formaldehyde are heated with 4—5 parts of alkali, the action is complete in a few minutes. E. W. W.

Acidic Properties of Starch. EM. DEMOUSSY (*Compt. rend.*, 1906, 142, 933—935).—The acidic properties of rice starch have been examined by allowing it to remain in contact with solutions of sodium, calcium, and barium hydroxides, of ammonia and sodium carbonate, and measuring the diminution of the alkali titre of the solutions. The diminution is considerable in the case of the hydroxide solutions, but much smaller with ammonia; the absorbed alkali can again be extracted with water. In the case of sodium carbonate, the diminution of the alkali titre is accompanied by the formation of an equivalent quantity of sodium hydrogen carbonate. Sodium chloride, potassium chloride, phosphate, and sulphate are all absorbed by starch. Copper acetate is absorbed to a much greater extent than the sulphate, and this is attributed to the weaker acid contained in it. Zinc and copper are taken up from ammoniacal solutions of the sulphates. The product obtained with copper is relatively stable; water extracts ammonia but no appreciable amount of copper from it. An ammoniacal solution of lead acetate shows no trace of dissolved lead after a few hours' contact with starch. Colloidal ferric oxide is also readily absorbed. The phenomena are attributed to the acidic character of the hydroxyl groups in the starch molecule. H. M. D.

[Hydrolysis of] some Celluloses. ADOLF ERNEST (*Zeit. Zuckerind. Böhm.*, 1906, 30, 279—282).—Sugar beet cellulose was dissolved in strong sulphuric acid (250 grams) and water (84 grams to 100 grams of substance), diluted with water until the strength of the acid was

4 per cent., and heated at 95—97°. Ramie cellulose was hydrolysed in a similar manner. Both substances yielded only dextrose.

N. H. J. M.

Compounds of Palladous Haloids with Aliphatic Amines. ALEXANDER GUTBIER and A. KRELL (*Ber.*, 1906, 39, 1292—1299. Compare Abstr., 1905, i, 876; ii, 584).—When a 33 per cent. solution of a primary aliphatic amine is added slowly to an excess of palladous chloride or bromide solution, a precipitate corresponding in composition with Vauquelin's salt, $\text{Pd}(\text{NH}_3)_4\text{X}_2 \cdot \text{PdX}_2$, is thrown down in the form of rose-red needles. Chlorides and bromides have been prepared by using methylamine, ethylamine, propylamine, and isobutylamine.

These salts are readily transformed into palladosammine derivatives; (1) when heated at about 200°; (2) when their aqueous solutions are evaporated; (3) by solution in warm alkali and precipitation with a solution of the requisite halogen hydride.

When solutions of the palladosammine chlorides or bromides are shaken with moist silver oxide, yellow solutions are obtained; these have a strongly alkaline reaction, can decompose ammonium salts, and contain the palladosammine hydroxides. All the palladosammine compounds are coloured: the chlorides pale yellow, the bromides dark yellow, and the iodides brownish-yellow. They all dissolve in concentrated ammonium hydroxide, yielding colourless solutions which contain palladosammine chloride, bromide, or iodide. The compounds are all of the type PdR_2X_2 , where R = a molecule of the amine and X = Cl, Br, or I. Those described contain methylamine, ethylamine, propylamine, isobutylamine, dimethylamine, and diethylamine. The iodides of the two last mentioned are extremely unstable and could not be isolated.

Double chlorides and bromides of the type $\text{PdCl}_2 \cdot 2\text{MeNH}_2 \cdot 2\text{HCl}$ have been prepared from methylamine, ethylamine, propylamine, and isobutylamine. They form red or reddish-brown crystals and are not decomposed by water.

J. J. S.

Decomposition of Urotropine (Hexamethylenetetramine) R. ISCHIDZU and T. INOUE (*Chem. Centr.*, 1906, i, 1087—1088; from *J. Pharm. Soc. Japan*, 1906, 1).—When urotropine, $\text{C}_6\text{H}_{12}\text{N}_4$, is decomposed by acids, the main products which contain carbon are formaldehyde and carbon dioxide. By the moderate action of hydrochloric or acetic acid for a certain time, urotropine (1 mol.) yields ammonia (2 mols.) and methylamine (2 mols.). When the concentration of the acid is increased, the temperature raised, or the duration of the action prolonged, the quantity of ammonia increases, whilst that of methylamine decreases. By distilling 100 parts of urotropine with dilute hydrochloric or sulphuric acid, ninety-five parts of formaldehyde are formed (theoretically 128); formaldehyde is also liberated by boiling with water. When urotropine is treated with saké, it is attacked by the free succinic, lactic, and acetic acids contained in the latter. When saké to which urotropine has been added is kept for some time, an appreciable quantity of formaldehyde is formed. Urotropine is more stable in alkaline than in neutral liquids.

E. W. W.

Glycine Picrate. PHOEBUS A. LEVENE (*J. Biol. Chem.*, 1906, 1, 413—414).—In the products of proteolysis, fractions containing glycine and alanine are easily obtained; from these, glycine is readily separable as a picrate; the method is stated to be simpler than Fischer's.

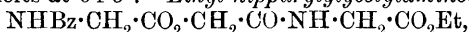
W. D. H.

Action of Nitrous Acid on Polyglycine Esters. I. Ethyl Diazoacetylaminooacetate. THEODOR CURTIUS and AUGUST DARAPSKY (*Ber.*, 1906, 39, 1373—1378).—*Ethyl diazoacetylaminooacetate*,



is obtained when a small quantity of acetic acid or dilute sulphuric acid is added to mixed concentrated solutions of sodium nitrite and ethyl glycylglycine hydrochloride at 0° . It separates from alcohol in yellow leaflets, melts at 107° , and resembles ethyl diazoacetate in its reactions. It is reduced to hydrazine by ferrous sulphate and sodium hydroxide, reacts with iodine in ethereal solution to form *ethyl di-iodoacetylaminooacetate*, $\text{CHI}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, melting at 127 — 128° , and is converted by boiling water into *ethyl hydroxyacetylaminooacetate*, $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, which separates from benzene in colourless prisms and melts at 68.5° .

Ethyl acetylglcylglycolylaminooacetate, $\text{OAc}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, obtained from ethyl diazoacetylaminooacetate and glacial acetic acid at 0° , forms colourless leaflets and melts at 88 — 89° . *Ethyl benzoylglcylglycolylaminooacetate*, $\text{OBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, obtained by heating the diazo-compound with benzoic acid on the water-bath, forms small needles and melts at 94.5° . *Ethyl hippurylglcylglycolylaminooacetate*,

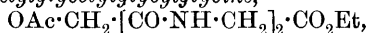


forms slender, glistening needles and melts at 88° .

Ethyl chloroacetylaminooacetate, obtained by passing hydrogen chloride into a dry ethereal solution of the diazo-compound, is identical with a substance described previously (Diels and Heintzel, *Abstr.*, 1905, i, 174).

C. S.

Action of Nitrous Acid on Polyglycine Esters. II Ethyl Diazoacetylglcylglycylaminooacetate. THEODOR CURTIUS and JAMES THOMPSON (*Ber.*, 1906, 39, 1379—1383).—*Ethyl diazoacetylglcylglycine*, $\text{N}_2\text{:CH}\cdot[\text{CO}\cdot\text{NH}\cdot\text{CH}_2]_2\cdot\text{CO}_2\text{Et}$, is obtained when sodium nitrite and a small quantity of acetic acid acts on a solution of ethyl diglycylglycine hydrochloride and sodium acetate at 0° . It crystallises from alcohol in glistening, yellow leaflets, melts at 159 — 160° , and is decomposed by dilute mineral acids with evolution of nitrogen. *Ethyl di-iodoacetylglcylglycylglycine*, $\text{CHI}_2\cdot[\text{CO}\cdot\text{NH}\cdot\text{CH}_2]_2\cdot\text{CO}_2\text{Et}$, prepared from an alcoholic solution of the preceding compound and iodine, separates from alcohol in yellow needles and melts at 169° . Ethyl chloroacetylglcylglycine, obtained from the diazo-compound and hydrogen chloride in alcoholic solution, is identical with the compound obtained by Fischer and Otto (*Abstr.*, 1903, i, 607). *Ethyl hydroxyacetylglcylglycylglycine*, $\text{OH}\cdot\text{CH}_2\cdot[\text{CO}\cdot\text{NH}\cdot\text{CH}_2]_2\cdot\text{CO}_2\text{Et}$, forms microscopic needles and melts at 108° . *Ethyl acetylglcylglycylglycylglycylglycine*,



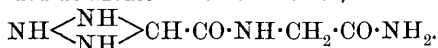
prepared from the diazo-compound and acetic acid, forms microscopic.

yellow crystals and melts at 124° . *Ethyl benzoylglycylglycylglycine*, $\text{OBz}\cdot\text{CH}_2\cdot[\text{CO}\cdot\text{NH}\cdot\text{CH}_2]_2\cdot\text{CO}_2\text{Et}$, melts at 131° . *Ethyl hippurylglycylglycylglycine*, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{CH}_2\cdot[\text{CO}\cdot\text{NH}\cdot\text{CH}_2]_2\cdot\text{CO}_2\text{Et}$, separates from hot water in colourless needles and melts at $148\text{--}149^{\circ}$.

Ethyl hippurylglycylglycylglycylglycine, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{CH}_2\cdot[\text{CO}\cdot\text{NH}\cdot\text{CH}_2]_2\cdot\text{CO}_2\text{Et}$, obtained from the diazo-compound and an alcoholic solution of hippurylglycine, crystallises from hot water in white needles and melts and becomes brown at $204\text{--}205^{\circ}$. C. S.

Action of Nitrous Acid on Polyglycine Esters. III. Action of Ammonia on Ethyl Diazoacetyl glycine and Ethyl Diazoacetyl glycylglycine. THEODOR CURTIUS and JAMES THOMPSON (*Ber.*, 1906, 39, 1383—1388. Compare Curtius and Gumlich, *Abstr.*, 1904, i, 477).—*Diazoacetyl glycineamide*, $\text{N}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, is precipitated when ammonia is passed into ice-cold water containing ethyl diazoacetyl glycine in suspension. It crystallises in yellow leaflets, melts and becomes brown at 160° , and is decomposed by dilute mineral acids or solutions of iodine with evolution of nitrogen. *Diazoacetyl glycylglycineamide*, $\text{N}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, similarly obtained, is a light yellow powder which melts and decomposes at 175° .

When excess of ammonium hydroxide is added to the foregoing amides or to the original esters without special cooling, colourless compounds are obtained with NH_3 which do not evolve nitrogen by treatment with mineral acids or solutions of iodine. They are provisionally regarded as azomethane derivatives, for example,



In cold concentrated aqueous solution they react with sodium nitrite and acetic acid to form an intensely violet solution from which ether extracts a substance which forms reddish-violet crystals, shows Liebermann's nitroso-reaction, and decomposes at 120° . C. S.

A New Type of Balanced Reactions. LOUIS J. SIMON (*Compt. rend.*, 1906, 142, 790—791. Compare *Abstr.*, 1902, i, 14).—The condensation of pyruvic acid and urethane to form diurethanepyruvic acid is a balanced reaction owing to the hydrolytic action of the water which forms the other product of the reaction. The dissociation of diurethanepyruvic acid by water increases (a) with the temperature; 100 c.c. of cold water require ten hours to hydrolyse 1.75 grams of the compound, whilst the reaction is completed in a few minutes at a gentle heat; (b) with the concentration, being complete in the most concentrated solutions, whilst solutions of lower concentrations contain equal numbers of dissolved and of dissociated molecules.

M. A. W.

Influence of the Juxtaposition of Ketonic and Acid Groups in the same Molecule. LOUIS J. SIMON (*Compt. rend.*, 1906, 142, 892—894).—Diurethanepyruvic acid, which is decomposed by water, dissolves in ethyl alcohol without decomposition. By means of the

alcoholic solution, the aniline, *p*-toluidine, and phenylhydrazine salts were prepared. The first two decompose at about 122° and 128°, the third melts without decomposing at 125°. When an aqueous solution of the phenylhydrazine salt is heated, the salt decomposes, the phenylhydrazone of pyruvic acid and urethane being formed.

Ethyl diurethanepyruvate, obtained by the action of hydrochloric acid on a mixture of pyruvic acid, urethane, and ethyl alcohol, is a crystalline substance which melts at 109°, distils without decomposition under reduced pressure, and dissolves readily in water. When heated with dilute acid, the ester is hydrolysed, and pyruvic acid, urethane, and alcohol are formed.

Potassium diurethanepyruvate, obtained by neutralising the acid, cannot be prepared by the action of urethane on potassium pyruvate. It is very soluble in water and ethyl alcohol, and contains $1\frac{1}{2}$ molecules of water of crystallisation which can be removed at 110—115°.

The observations show the influence of the juxtaposition of the ketonic and acid groups.

H. M. D.

Ketone-cyanohydrins. HANS BUCHERER and ANDRÉ GROLÉE (*Ber.*, 1906, **39**, 1224—1227. Compare Abstr., 1903, i, 612).— α -Hydroxyisobutyronitrile and ethyl β -cyano- β -hydroxybutyrate are formed by the action of potassium cyanide on the sodium hydrogen sulphite compounds of acetone and ethyl acetoacetate in concentrated aqueous solution in yields of 96 per cent. and 97 per cent. of the theoretical respectively.

When pure, ethyl β -cyano- β -hydroxybutyrate is a reddish-yellow, heavy oil, which has no odour of hydrogen cyanide and is more stable than previously supposed (Morris, *Trans.*, 1880, **37**, 6; Schiller-Wechsler, *Abstr.*, 1885, 900).

G. Y.

Dialkylmalonamides. KARL BÖTTCHER (*Ber.*, 1906, **39**, 1596. Compare Meyer, this vol., i, 137).—Better yields of the amides are obtained from the chlorides when the temperature is kept below 20°. The formation of α -methylbutyramide observed by Meyer was probably due to the presence of α -methylbutyryl chloride in the chloride used.

J. J. S.

Solubility of Uric Acid in Silicic Acid, in Sodium Metasilicate, and in Distilled Water. EZIO COMANDUCCI (*Chem. Centr.*, 1906, i, 1091; from *Boll. Chim. Farm.*, **45**, 108—111).—Distilled water dissolves a larger quantity of uric acid in a day than water which contains 0.076 per thousand of silica or 0.12 of sodium silicate, Na_2SiO_3 . The results of Gauthier's determinations of the solubility of uric acid in Mangiatorella water (*Calabria, Avanti!* 1904, 15 Sept.) may possibly be explained by the slow decomposition of the uric acid during the experiment and the subsequent solution of the decomposition products.

E. W. W.

Action of Certain Gases on Potassium Thiocyanate at High Temperatures. JAROSLAV MILBAUER (*Zeit. anorg. Chem.*, 1906, **49**, 46—57. Compare Abstr., 1905, i, 121).—Potassium thiocyanate

only undergoes slight dissociation into potassium cyanide and sulphur when kept for some hours at a bright red heat under diminished pressure. A similar result is obtained by heating in nitrogen and in carbon monoxide; these gases have no chemical action on the salt. In an atmosphere of hydrogen at a low red heat, decomposition occurs in approximate accordance with the equation: $4\text{KCNS} + 4\text{H}_2 = 2\text{KCN} + \text{K}_2\text{S} + 3\text{H}_2\text{S} + 2\text{HCN}$. The salt is also decomposed by water vapour at a high temperature with formation of potassium sulphide and carbonate and evolution of carbon dioxide, hydrogen sulphide, and ammonia. When heated in hydrogen sulphide, potassium cyanide, hydrogen cyanide, and sulphur are produced; in carbon dioxide at a low red heat, a little potassium cyanate is formed. The action of sulphur dioxide on the thiocyanate takes place in the following two stages: $2\text{KCNS} + 2\text{SO}_2 = \text{K}_2\text{S} + 2\text{CO}_2 + \text{N}_2 + 3\text{S}$ and $\text{K}_2\text{S} + 2\text{SO}_2 \rightleftharpoons \text{K}_2\text{SO}_4 + 2\text{S}$; the second reaction is reversible. G. S.

Complex Mercury Cobalt and Mercury Nickel Thiocyanates.

E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 1269—1272).—The salts described by the author were prepared by dissolving mercuric chloride and ammonium (or potassium) thiocyanate in water and adding to the compound, $(\text{NH}_4)_2\text{Hg}(\text{CNS})_4$, thus formed, a solution of cobalt nitrate (or sulphate) or nickel nitrate.

The *cobalt* salt, $\text{CoHg}(\text{CNS})_4$, forms beautiful blue crystals slightly soluble in water. Dilute hydrochloric or sulphuric acid has only little action on it, but aqueous alkali hydroxides decompose it, giving cobalt hydroxide and mercuric oxide. It may be used as a mineral pigment.

The *nickel* salt, $\text{NiHg}(\text{CNS})_4$, $\text{Hg}(\text{CNS})_2$, which is readily soluble in aqueous ammonium or potassium thiocyanate, forms a bluish-green powder.

Mixed nickel and cobalt salts of a dark green colour can also be obtained. T. H. P.

Absorption Spectra of Solutions of Isomeric Complex Cobalt

Salts. ARTHUR ROSENHEIM and VICTOR J. MEYER (*Zeit. anorg. Chem.*, 1906, **49**, 28—33).—As ammonium thiocyanate and thiocarbamide are isomeric, the *dithiocarbamide cobalt thiocyanate*, $\text{Co}(\text{CSN}_2\text{H}_4)_2(\text{SCN})_2$, described by the authors (see this vol., i, 408) is isomeric with the *ammonium cobalt thiocyanate*, $(\text{NH}_4)_2\text{Co}(\text{SCN})_4$, referred to in previous papers. For this reason it has been considered of interest to compare the absorption spectra of these two compounds dissolved in absolute alcohol.

The spectra of solutions of ammonium cobalt thiocyanate from 1/16 to 1/512 normal are qualitatively identical; there is no displacement of the region of absorption. It is considered that the absorptive power pertains to the bivalent ion $\text{Co}(\text{SCN})_4^{++}$, which remains stable on dilution. The isomeric dithiocarbamide cobalt thiocyanate shows an entirely different spectrum; the positions of maximum absorption vary greatly with the dilution, and in 1/128 normal solutions the absorptive power has practically disappeared. With the object of throwing light on the nature of the absorbing groups, measurements were also made with cobalt chloride hexahydrate and cobalt thiocyanate

in alcoholic solution, and it was found that the spectrum of the latter salt closely resembles that of ammonium cobalt thiocyanate, whilst the entirely different spectrum of cobalt chloride corresponds in certain dilutions with that of the thiocarbamide compound. The authors discuss the bearing of these results, which are not entirely in accordance with present views as to the condition of cobalt salts in solution (compare Donnan and Bassett, *Trans.*, 1902, **81**, 939).

Photographs of the different spectra are given in the paper.

G. S.

Compounds of Thiocarbamide and of Xanthamide with Salts of Univalent Copper. ARTHUR ROSENHEIM and WILHELM STADLER (*Zeit. anorg. Chem.*, 1906, **49**, 1—12. Compare *Abstr.*, 1903, i, 325; Kohlschütter, *ibid.*, 468).—In a former paper (*loc. cit.*), complex salts of the types $\text{Cu}(\text{CH}_4\text{N}_2\text{S})\text{X}$, $\text{Cu}(\text{CH}_4\text{N}_2\text{S})_2\text{X}$, and $\text{Cu}(\text{CH}_4\text{N}_2\text{S})_3\text{X}$ (X = univalent anion) have been described; the results of some further experiments on the constitution of these salts are now given. It had already been observed that the electrical conductivity of salts of the last type increased abnormally on dilution; from a comparison of the conductivities of aqueous solutions of $\text{Cu}(\text{CH}_4\text{N}_2\text{S})_3\text{Cl}$ and of the compound, $[\text{Cu}(\text{CH}_4\text{N}_2\text{S})_2\text{H}_2\text{O}]\text{NO}_3$, described by Kohlschütter, the conclusion is drawn that the abnormal results referred to are due to hydrolysis of the tri-derivatives according to the equation $\text{Cu}(\text{CH}_4\text{N}_2\text{S})_3\text{X} + \text{H}_2\text{O} = [\text{Cu}(\text{CH}_4\text{N}_2\text{S})_2\text{H}_2\text{O}]\text{X} + \text{CH}_4\text{N}_2\text{S}$. Contrary to Kohlschütter's contention, the compound $\text{Cu}(\text{CH}_4\text{N}_2\text{S})_3\text{Cl}$ is precipitated unchanged from aqueous solution by metallic chlorides; no satisfactory explanation of this behaviour has been found.

Complex salts of univalent copper with xanthamide, of the types $\text{Cu}(\text{NH}_2\cdot\text{CS}\cdot\text{OEt})\text{X}$, $\text{Cu}(\text{C}_3\text{H}_7\text{ONS})_2\text{X}$, and $\text{Cu}(\text{C}_3\text{H}_7\text{ONS})_3\text{X}$ (X = halogen atom) have been obtained by interaction of the components dissolved in absolute alcohol. $\text{Cu}(\text{C}_3\text{H}_7\text{ONS})\text{Cl}$ forms small, lustrous pyramids which melt at 126—127°; $\text{Cu}(\text{C}_3\text{H}_7\text{ONS})_2\text{Cl}$ occurs in slender, colourless needles melting at 119°; $\text{Cu}(\text{C}_3\text{H}_7\text{ONS})_3\text{Cl}$ forms crystalline plates melting at 111°. The corresponding *bromides* and *iodides* were also obtained in crystalline form.

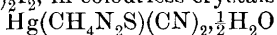
With the object of throwing further light on the constitution of the xanthamide compounds, molecular weight determinations by the boiling point method were made in different solvents, but the results were not very conclusive. In benzene solution, the tri-derivatives seem to be split up into mono- or di-derivatives and the free base, whilst the di-derivatives have double the normal molecular weight. Conductivity measurements in absolute alcohol show that the mono-derivatives are most highly ionised under these conditions.

G. S.

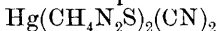
Compounds of Thiocarbamide with Salts of Bivalent Metals. ARTHUR ROSENHEIM and VICTOR J. MEYER (*Zeit. anorg. Chem.*, 1906, **49**, 13—27. Compare preceding abstract).—The majority of the complex salts here described were obtained by interaction of varying proportions of their components in aqueous solution. It is shown by solubility and electrical conductivity measurements that the

stability of these compounds decreases in the order : Hg, Pb, Cd, Zn, Co, Ni, Fe, Mn, Ca, in approximate agreement with the theory of electro-affinity of Abegg and Bodländer.

Mercury Compounds.— $\text{Hg}(\text{CH}_4\text{N}_2\text{S})\text{Cl}_2, \frac{1}{2}\text{H}_2\text{O}$ occurs in small, well-formed needles melting at 234° ; $\text{Hg}(\text{CH}_4\text{N}_2\text{S})_2\text{Cl}_2$ forms a microcrystalline precipitate melting at 250° ; $\text{Hg}(\text{CH}_4\text{N}_2\text{S})_4\text{Cl}_2$ separates from water in large, prismatic crystals, which decompose above 180° . $\text{Hg}(\text{CH}_4\text{N}_2\text{S})\text{I}_2$ occurs as a yellow, microcrystalline precipitate melting at 135° ; $\text{Hg}(\text{CH}_4\text{N}_2\text{S})_2\text{I}_2$, in colourless crystals;



forms colourless scales which decompose above 160° ;



forms long, colourless needles melting at 181° ; $\text{Hg}(\text{CH}_4\text{N}_2\text{S})_2(\text{SCN})_2$ crystallises from alcohol in colourless needles.

Lead Compounds.—The compound $\text{Pb}(\text{CH}_4\text{N}_2\text{S})_2\text{Cl}_2$ forms long, colourless needles; the corresponding bromide occurs in yellowish-white needles, and the iodide in deep yellow needles. The compound $\text{Pb}(\text{CH}_4\text{N}_2\text{S})_4(\text{SCN})_2$ also occurs in colourless needles. Two complex nitrates, $\text{Pb}_2(\text{CH}_4\text{N}_2\text{S})_2(\text{NO}_3)_2$ and $\text{Pb}_2(\text{CH}_4\text{N}_2\text{S})_{11}(\text{NO}_3)_4$ were also obtained; the former occurs in large, well-formed prisms, the latter in long, colourless needles.

Cadmium Compounds.— $\text{Cd}(\text{CH}_4\text{N}_2\text{S})_2\text{Cl}_2$ occurs in long, colourless needles, $\text{Cd}(\text{CH}_4\text{N}_2\text{S})_2(\text{SCN})_2$ in short, yellowish-white needles, and $\text{Cd}(\text{CH}_4\text{N}_2\text{S})_3\text{SO}_4$ in colourless prisms.

Zinc Compounds.— $\text{Zn}(\text{CH}_4\text{N}_2\text{S})_4(\text{NO}_3)_2$ forms colourless, lustrous plates; $\text{Zn}(\text{CH}_4\text{N}_2\text{S})_2(\text{SCN})_2$ forms small needles; $\text{Zn}(\text{CH}_4\text{N}_2\text{S})_3\text{SO}_4$ occurs in colourless, tabular crystals.

Cobalt Compounds.— $\text{Co}_2(\text{CH}_4\text{N}_2\text{S})_7\text{Cl}_4$ forms bluish-black crystals; $\text{Co}(\text{CH}_4\text{N}_2\text{S})_4(\text{NO}_3)_2$, deep bluish-green crystals; $\text{Co}(\text{CH}_4\text{N}_2\text{S})_3(\text{SO}_4)_2$, a deep blue, crystalline powder; $\text{Co}(\text{CH}_4\text{N}_2\text{S})_2(\text{SCN})_2$, lustrous, brown needles.

Nickel Compounds.— $\text{Ni}_2(\text{CH}_4\text{N}_2\text{S})_7\text{Cl}_4$ forms beautiful, yellowish-brown crystals; $\text{Ni}(\text{CH}_4\text{N}_2\text{S})_5(\text{NO}_3)_2$, greenish-yellow prisms;



greenish-yellow needles. The cobalt and nickel compounds are relatively stable in alcohol solution, but are immediately decomposed by water.

Iron and Manganese Compounds.— $\text{Fe}(\text{CH}_4\text{N}_2\text{S})_4\text{Cl}_2$ occurs in green crystals; $\text{Fe}(\text{CH}_4\text{N}_2\text{S})_3(\text{SCN})_2$ in slender, green needles;



is obtained from an alcoholic solution in colourless, glistening plates; $\text{Mn}(\text{CH}_4\text{N}_2\text{S})_2(\text{SCN})_2$ forms yellowish-white, slender needles.

The only well-defined compound so far obtained with salts of the alkaline earths is $\text{Ca}(\text{CH}_4\text{N}_2\text{S})_5\text{Cl}_2, 6\text{H}_2\text{O}$; it occurs in long needles, and is completely split up into its components in aqueous solution.

G. S.

Action of Xanthates on Derivatives of Chloroacetic Acid.
HEINRICH FRERICHES and O. RENTSCHLER (*Arch. Pharm.*, 1906, 244, 77—85).—Sodium benzylxanthate was prepared by treating benzyl

alcohol with sodium, suspending the product in ether, and adding carbon disulphide gradually.

By heating potassium or sodium alkylxanthates, $OR \cdot CS \cdot SM$ [$R = Me, Et, Pr, CH_2Ph$; $M = K, Na$] with chloroacetylcarbamides, $CH_2Cl \cdot CO \cdot NH \cdot CO \cdot NHR'$ [$R' = H, Me$], ethyl chloroacetylcarbamate, $CH_2Cl \cdot CO \cdot NH \cdot CO \cdot OEt$, or chloroacetylarylamines, $CH_2Cl \cdot CO \cdot NR''R'''$ [$R'' : R''' = H : Ph, Me : Ph, CH_2Ph : Ph, H : C_6H_4Me$ *p* and *m*, *Ph : Ph, H : C_6H_4 \cdot OMe* *o*], in alcoholic solution, xanthylacetyl-carbamides, ethyl-carbamates, and -arylamides are obtained, of the type $OR \cdot CS \cdot S \cdot CH_2 \cdot CO \cdot NH \cdot CO \cdot NHR'$, $OR \cdot CS \cdot S \cdot CH_2 \cdot CO \cdot NH \cdot CO \cdot OEt$, or $OR \cdot CS \cdot S \cdot CH_2 \cdot CO \cdot NR''R'''$ respectively. They are enumerated below, with their melting points.

Xanthylacetylcarbamides [$R' = H$]: *methyl-, ethyl-, propyl-, benzyl-* [$R' = Me, Et, Pr, CH_2Ph$]; 170—171°, 177—178°, 168—169°, 165° respectively. *Xanthylacetylmethylcarbamides* [$R' = Me$]: *methyl-, ethyl-, propyl-, benzyl-* [$R' = Me, Et, Pr, CH_2Ph$]; 176°, 185°, 175—176°, 189—190°.

Ethylxanthylacetylcarbamates: *methyl-, ethyl-, propyl-* [$R = Me, Et, Pr$]; 92—93°, 103—104°, 93—94°.

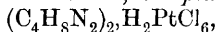
Xanthylacetoanilides [$R'' : R''' = H : Ph$]: *methyl-, ethyl-, propyl-* [$R = Me, Et, Pr$]; 190—191°, 98—99°, 86—87°. *Ethylxanthylacetomethylanilide* and *-benzylanilide* [$R : R'' : R''' = Et : Me : Ph, Et : CH_2Ph : Ph$];

85—86°, 65—66°. *Xanthylaceto-p-toluidides* [$R'' : R''' = H : C_6H_4Me$]: *methyl-, ethyl-, propyl-* [$R = Me, Et, Pr$]; 164—165°, 136°, 132—133°; *ethylxanthylacetodiphenylamide* 82°. *Ethylxanthylacetodiphenylamide* [$R : R'' : R''' = Et : Ph : Ph$], 111°. *Ethylxanthylacetodiphenylamide* [$R : R'' : R''' = Et : H : C_6H_4 \cdot OMe$], 53—54°. C. F. B.

Action of Ammonium Cyanide on the Saturated Ketones. WLADIMIR VON GULEWITSCH and TH. WASMUS (*Ber.*, 1906, 39, 1181—1194. Compare Gulewitsch, *Abstr.*, 1900, i, 476).—Amino-nitriles together with the corresponding amino-acids are formed with development of heat by the action of a small excess of ammonium cyanide on ketones of the limit series in alcoholic or alcoholic-etheral solution (Ljubawin, *Abstr.*, 1883, 178; Jay and Curtius, *Abstr.*, 1894, i, 162). The best yields are obtained when the reaction takes place at the ordinary temperature for twenty hours or at 60—70° for two hours under pressure. The percentages given are those of the theoretical yields of the hydrochlorides of the aminonitriles and the copper salts of the amino-acids, in which forms the products are isolated. The aminonitriles formed from the ketones of the limit series differ from those formed from aldehydes, in that they distil without decomposing under small pressures.

α-Aminoisobutyronitrile (compare Hellsing, *Abstr.*, 1904, i, 563), prepared from acetone, boils at 49—50° (corr.) under 12 mm. pressure, has a sp. gr. 0.8899 at 16.9°/4°, and is readily soluble in water, alcohol, ether, or benzene; the aqueous solution turns litmus blue. The aminonitrile remains almost unchanged in a closed vessel for four months, but on exposure to air, in seven days it commences to deposit stellate aggregates of thin needles, and changes

finally into a crystalline mass. When reduced with sodium and alcohol, it yields isopropylamine, ammonia, and hydrogen cyanide or formic acid. The *hydrochloride*, $C_4H_8N_2 \cdot HCl$ (55 per cent.), crystallises from a mixture of alcohol and ether in tetragonal or hexagonal plates, more seldom in needles, melts and decomposes at $144-146^\circ$, and has an acid reaction in aqueous solution; the *platinichloride*,



was analysed.

α-Benzoylaminoisobutyronitrile, $NHBz \cdot CMe_2 \cdot CN$, crystallises from alcohol in long, glistening needles and melts at 168.5° . *α-Amino-isobutyramide hydrochloride*, $NH_2 \cdot CO \cdot CMe_2 \cdot NH_2 \cdot HCl$, is formed when the aminonitrile hydrochloride is dissolved in fuming hydrochloric acid; it crystallises in stout prisms, becomes opaque on exposure to air, and when recrystallised from water is converted for the greater part into *α-aminoisobutyric acid*, which is formed also by boiling the aminonitrile with hydrochloric acid.

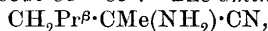
The action of ammonium cyanide on methyl ethyl ketone in aqueous solution leads to the formation of *α-amino-α-methylbutyric acid* (Slimmer, Abstr., 1902, i, 206).

The *copper* and *nickel* salts are described.

α-Amino-α-ethylbutyronitrile hydrochloride, $CN \cdot CEt_2 \cdot NH_2 \cdot HCl$ (40 per cent.), formed together with copper *α-amino-α-ethylbutyrate* (6 per cent.) from diethyl ketone, is obtained as a white, crystalline powder and melts at $110-113^\circ$. The *aminonitrile*, $C_6H_{12}N_2$, has a strong odour of camphor, boils at $70.8-71.7^\circ$ (corr.) under 11 mm. pressure, and has a sp. gr. 0.8934 at $15.6^\circ/4^\circ$.

α-Amino-α-methylhexonitrile hydrochloride, $C_7H_{14}N_2 \cdot HCl$ (51 per cent.), is obtained from methyl butyl ketone as a white powder, and melts at about $90-93^\circ$. The *aminonitrile*, $CH_2Pr^{\alpha} \cdot CMe(NH_2) \cdot CN$, boils at $86-88^\circ$ (corr.) under 10 mm. pressure, and has an odour resembling that of *α-amino-α-ethylbutyronitrile*. *Copper α-amino-α-methylhexoate*, $C_{14}H_{28}O_4N_2Cu \cdot 2H_2O$ (37 per cent.), crystallises in blue needles or small prisms having a violet tint.

α-Amino-α-methylisohexonitrile hydrochloride, $C_7H_{14}N_2 \cdot HCl$ (53 per cent.), formed together with the copper salt of the amino-acid (10 per cent.) from methyl isobutyl ketone, is obtained as a white, crystalline powder and melts at about $83-85^\circ$. The *aminonitrile*,



boils at $74.5-76^\circ$ (corr.) under 10 mm. pressure, and when reduced with sodium and alcohol yields *δ-amino-β-methylpentane*.

Copper α-amino-α-methylisohexoate, $C_{14}H_{28}O_4N_2Cu$, crystallises in small, light blue leaflets.

α-Amino-α-tert.-butylacetoneitrile hydrochloride, $C_7H_{14}N_2 \cdot HCl$ (34 per cent.), formed together with the copper salt of the amino-acid (8 per cent.) from pinacolin, melts and decomposes at $155-156^\circ$.

α-Amino-α-methyloctonitrile hydrochloride, $C_9H_{18}N_2 \cdot HCl$ (55 per cent.), formed together with the copper salt of the amino-acid (29 per cent.) from methyl hexyl ketone, melts at about $104-106^\circ$.

α-Amino-α-methyloctioic acid, $C_8H_{16} \cdot CMe(NH_2) \cdot CO_2H$, crystallises in small, greasy leaflets, sublimes but does not melt, and is only sparingly soluble in cold water, but is readily so in hot water or alcohol. G. Y.

Mercuric Oxycyanide. KARL HOLDERMANN (*Arch. Pharm.*, 1906, 244, 133—136).—The molecular weight in aqueous solution, determined cryoscopically, is rather less than half that corresponding with the formula $O(Hg \cdot CN)_2$, although the substance is extremely little dissociated electrolytically (this vol., i, 75). As the solution has an alkaline reaction, it is probable that when the substance dissolves in water it reacts with the latter to form $2OH \cdot Hg \cdot CN$, which is slightly dissociated into the ions $\cdot OH$ and $\cdot Hg \cdot CN$. It gives no precipitate with silver nitrate, and therefore it can hardly form the ions $\cdot Hg \cdot O \cdot Hg \cdot$ and $2 \cdot CN$, as suggested by Rupp (this vol., i, 340).

Mercuric oxycyanide is prepared more conveniently by the following method than by those described previously (compare Prussia, *Abstr.*, 1899, i, 319). Dissolve 125 grams of mercuric acetate and 105 grams of mercuric cyanide in about 1 litre of nearly boiling water; filter if necessary; stir constantly, and add approximately normal aqueous sodium hydroxide until a drop of the liquid reddens phenolphthalein paper (about 890 c.c. will be required; the approach of the end-point is indicated by the sudden crystallisation of the oxycyanide). Allow to remain a day in the cold, filter, wash with cold water, and dry in the air. The mother liquor may be used once more to dissolve the same quantities of mercuric salts. C. F. B.

Constitution and Method of Formation of Trimolecular Nitriles or Cyanalkines. ERNST VON MEYER (*Chem. Centr.*, 1906, i, 941—942; from *Ber. k. Sächs. Ges. Wiss.*, 57, 324—352. Compare *Abstr.*, 1905, i, 155).—The paper consists for the most part of a summary of work which has already been published in reference to the trimolecular nitriles or cyanalkines, together with an account of the methods of formation and probable constitution of these compounds. *Phthalyl cyanethine*, $C_9H_{13}N_2N(CO)_2C_6H_4$, prepared by the action of phthalic acid on cyanethine, crystallises in white needles and melts at 127.5° . Unlike the alkyl derivatives, the acyl derivatives readily regenerate cyanethine. *Tribromocyanethine* forms lustrous leaflets and melts at 126° .

By the action of sodium on ethyl cyanide in ethereal solution, a solid product is formed which contains sodium cyanethine, cyanethine, sodium ethyl cyanide, and sodium cyanide; sodium propionate and ammonia are formed by secondary reactions. Ethyl cyanide yields about 60 per cent. of cyanethine, but when lithium is used instead of sodium the yield increases to 80; when potassium is used, however, it sinks to 20—25 per cent. Magnesium does not attack the cyanide except when in the active condition and at a very high temperature. When sodamide is used instead of sodium, the reduction of ethyl cyanide and the secondary reactions which result in the formation of sodium cyanide and ethane do not occur; successful experiments were made with ethyl, methyl, benzyl, and phenyl cyanides. Sodium alkyl oxides, but not the phenoxide, cause polymerisation of the alkyl cyanides, especially when heated at 130 — 140° with the cyanide which contains the same alkyl group, a constant equilibrium between the cyanalkine, sodium alkyl cyanide, alcohol, and alkyl cyanide being probably attained. Ethyl

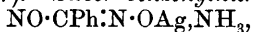
cyanide is also converted into cyanethine when heated with commercial sodium cyanamide, zinc ethyl, or anhydrous barium oxide.

E. W. W.

Influence of the Added Substance on Substitution in Aromatic Nuclei. ARNOLD F. HOLLEMAN (*Ber.*, 1906, 39, 1715—1716).—The partial nitration of nitrobenzene at 30° yields a mixture of 91.1 per cent. of meta-, 8.3 per cent. of ortho-, and 0.6 per cent. of para-dinitrobenzene. The mixture obtained after complete nitration consists of 90.9 per cent. of meta-, 8.1 per cent. ortho-, and 1.0 per cent. of para-dinitrobenzene. *p*-Nitroacetanilide is the sole product of the nitration of acetanilide by dilute nitric acid; the more concentrated the acid, the greater the yield of dinitroacetanilide. The results of experiments on the nitration of nitrobenzene and of benzoic acid in the presence and absence of sulphuric acid are also quoted.

C. S.

Benzenylnitrosolic Acid. HEINRICH WIELAND and HUGO BAUER (*Ber.*, 1906, 39, 1480—1488. Compare Wieland, *Abstr.*, 1905, i, 420; Ley, *Abstr.*, 1898, i, 657).—*Silver benzenylnitrosolate*,



is prepared by adding 8 per cent. ammonia to benzoylhydroxylaminoxime in ethereal solution, and treating the resulting solution with silver nitrate. It crystallises in unstable, matted, glistening, rose-red needles, decomposes at 94° forming ammonia, silver, benzonitrile, nitrogen peroxide, and water, detonates when heated on platinum, forms a silver mirror when boiled with water, and gives Liebermann's reaction. It is only sparingly soluble in dilute ammonia, but dissolves in moderately concentrated ammonia forming the blue *ammonium* salt, liberates iodine from potassium iodide in acid aqueous solution, and diazotises aniline in hydrochloric acid solution. The deep blue solution of the *potassium* salt is obtained when the silver salt is shaken with potassium iodide solution; with copper acetate, the ammoniacal solution forms a dark brown copper salt which rapidly decomposes, yielding an odour of benzonitrile. The free *acid* is obtained as an unstable, pale green film when the blue ammoniacal solution is treated with ether and acetic acid, and the resulting green ethereal solution is evaporated in a vacuum.

Benzenylamino-oxime, which is formed together with benzenylnitrosolic acid by the action of ammonia on benzoylhydroxylamino-oxime in ethereal solution, is obtained also by the reduction of the blue ammoniacal solution of benzenylnitrosolic acid with hydrogen sulphide.

Dibenzenyloxazoxime, $\text{CPh} \begin{smallmatrix} \text{O} \cdot \text{N} \\ \text{NO} \end{smallmatrix} \text{CPh}$, is formed by the action

of dilute nitric or hydrochloric acid on the ammoniacal solution of benzenylnitrosolic acid cooled by ice; it crystallises from petroleum in large, pale yellow, feathery plates or leaflets, melts and decomposes at 130—131°, dissolves readily in alcohol, benzene, or chloroform, gives a slight coloration with ferric chloride, and is decomposed, forming benzonitrile and benzoic and nitrous acids, when boiled with aqueous alkali hydroxides or acids; when reduced with zinc dust and glacial acetic acid in boiling alcoholic solution, it yields dibenzenyloxime. The action

of iodine on silver benzenylnitrosolate suspended in ether leads to the formation of diphenylglyoxime peroxide. G. Y.

Sulphonic Esters of Hydroxybenzaldehydes and Hydroxybenzoic Acids. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 162322).—The esters of the formula $C_6H_4Me \cdot SO_3R$, obtained from cresols and aromatic sulphonic acids, are readily oxidised by means of manganese dioxide and sulphuric acid to the corresponding aldehydic esters, $CHO \cdot C_6H_4 \cdot SO_3R$, from which the hydroxybenzaldehydes are obtained on hydrolysis.

The tolyl esters are obtained by the action of arylsulphonic chlorides on warm dilute alkaline solutions of the cresols (compare Georgescu, Abstr., 1900, i, 343). The following are the melting points:

	<i>o</i> -Tolyl	<i>p</i> -Tolyl	<i>m</i> -Tolyl
<i>Benzenesulphonic</i>	35—36°	43°	45°
<i>p-Toluenesulphonic</i>	52°	67—68°	48°
<i>o-Toluenesulphonic</i>	50—51°	70—71°	60°

The hydroxybenzaldehydesulphonic acids obtained on oxidation are crystalline compounds, insoluble in water, but dissolving in organic solvents. They yield additive compounds with sodium hydrogen sulphite, and condense with dimethylaniline and zinc chloride to form the leuco-compounds of dyes. Melting points:

	<i>o</i> -	<i>p</i> -	<i>m</i> -
<i>Benzenesulphonic</i>	54—55°	82°	liquid
<i>p-Toluenesulphonic</i>	62°	73—74°	66—68°
<i>o-Toluenesulphonic</i>	79—80°	61—62°	65—66°

The corresponding carboxylic acids are obtained in small quantity at the same time.

	<i>o</i> -	<i>p</i> -	<i>m</i> -
<i>Benzenesulphonic</i> ...	130°	170°	114—116°
<i>p-Toluenesulphonic</i> ...	154—156°	168—170°	162°
<i>o-Toluenesulphonic</i> ...	118—120°	168—170°	144—146°.

C. H. D.

Nitrostilbene. PAUL PFEIFFER and J. MONATH (*Ber.*, 1906, **39**, 1304—1307).—2-Nitrostilbene was prepared by a method differing slightly from that recently described by Sachs and Hilpert (this vol., i, 241). 2:4-Dinitrostilbene was reduced to 2-nitro-4-aminostilbene, which was diazotised in dilute hydrochloric acid solution; the properties of 2-nitrostilbene, obtained by the action of alkaline stannous chloride on the diazonium chloride, agreed with those assigned to it by Sachs and Hilpert (*loc. cit.*).

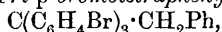
2:6-Dinitrostilbene, prepared by the condensation of 2:6-dinitrotoluene with benzaldehyde in the presence of a little piperidine, separates from benzene in yellow needles and melts at 86°.

2:4:6-Trinitrostilbene, prepared by the condensation of 2:4:6-trinitrotoluene with benzaldehyde in the presence of a little piperidine, separates from benzene in bright yellow, glistening plates or leaflets of

the *benzene additive compound*; the latter melts at 158° and loses benzene in the air. A. McK.

Triphenylmethyl. XIII. MOSES GOMBERG and LEE H. CONE (*Ber.*, 1906, **39**, 1461—1470).—Tetraphenylmethane may be readily prepared by the action of magnesium phenyl bromide on triphenylchloromethane in ethereal solution. The yield varies from 5 to 10 per cent., and other products formed are triphenylmethane and the corresponding carbinol, and triphenylmethyl peroxide.

A good yield of $\alpha\beta\beta\beta$ -tetraphenylethane, $\text{CPh}_3\cdot\text{CH}_2\text{Ph}$, is obtained by the action of magnesium benzyl chloride on triphenylchloromethane. It crystallises from a mixture of ether and light petroleum in large, transparent, monoclinic prisms, and melts at 144°. When oxidised with chromic acid, it yields triphenylcarbinol. *p*-Chlorotetraphenylethane, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CPh}_2\cdot\text{CH}_2\text{Ph}$, obtained by condensing magnesium benzyl chloride with *p*-chlorotriphenylchloromethane, melts at 156°. The corresponding 2:4':4"-trichloro-derivative, $\text{C}(\text{C}_6\text{H}_4\text{Cl})_3\cdot\text{CH}_2\text{Ph}$, obtained from 2:4':4"-trichlorotriphenylchloromethane (*Abstr.*, 1904, i, 489), melts at 140°. *Tri-p-bromotetraphenylethane*,

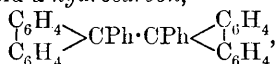


melts at 201°.

Kuntze-Fechner's *aaa*-triphenylethane (*Abstr.*, 1903, i, 244) is obtained by condensing triphenylchloromethane with magnesium methyl iodide, and Fischer's *aaa*-triphenylpropane (*Annalen*, 1878, 194, 261) may be prepared by a similar method.

Pentaphenylethane, $\text{CHPh}_2\cdot\text{CPh}_3$, may be prepared by the action of Bayer's active magnesium (*Abstr.*, 1905, i, 766) on a mixture of diphenylbromomethane and triphenylchloromethane in ethereal solution. It crystallises from light petroleum of high boiling point in colourless plates, begins to soften at 165°, is completely molten at 175—180°, and dissolves sparingly in ether, alcohol, or light petroleum.

Phenyl diphenylene chloromethane and molecular silver in the presence of benzene yield a *hydrocarbon*,



melting at 193°.

J. J. S.

Observations on Coal Tars. ERNST BORNSTEIN (*Ber.*, 1906, **39**, 1238—1242. Compare *Abstr.*, 1903, i, 166).—The tar obtained from a Westphalian coal has been examined. The amount formed at temperatures up to 450° is extremely small, only 9 grams per kilo. of coal. It has a sp. gr. 1.03 and contains C = 88.3, H = 7.8, and O = 2.2 per cent. It does not contain paraffins or naphthalene, but *isomethylanthracene* (*Abstr.*, 1883, 70).

When the coal is heated to 500°, the yield of tar is 2.06 grams per 100 grams of coal, of which some 30 per cent. distils above 350°.

Another component of the tar is the hydrocarbon crackene, $\text{C}_{24}\text{H}_{18}$ (*Abstr.*, 1900, i, 284). These two hydrocarbons appear to be characteristic of tars obtained at moderate temperatures from coals rich in carbon. J. J. S.

Pseudo-acids. HANS EULER (*Ber.*, 1906, **39**, 1607—1615. Compare Hantzsch, *Abstr.*, 1899, i, 399; 1904, i, 381, 725; von Zawidski, 1904, i, 232, 475; Johnston, *ibid.*, i, 984).—The group of pseudo-acids discussed comprises the compounds which exhibit neither slow neutralisation nor abnormal hydrolysis, for example, phenylnitroamine and violuric acid. Electrical conductivity determinations gave the following results for $K \times 10^6$ at 18° :

	Water.	44 per cent. alcohol.
Phenylnitroamine	17.5	1.26
Acetic acid	17.8	1.86

The temperature-coefficient for K is somewhat larger than that for acetic and benzoic acids and their homologues and increases with the temperature, but only to somewhat the same extent as for other feeble electrolytes, such as phenol and aniline, and for nitrogen acids such as aminotetrazole. The behaviour of phenylnitroamine towards ammonia in perfectly dry benzene solution is quite analogous to that of benzoic acid, and the conclusion is drawn that so far no physico-chemical proofs of molecular rearrangement of phenylnitroamine during ionisation or salt formation are available.

Conductivity determinations of solutions of aniline acetate and aniline violurate indicate that the two salts are hydrolysed to much the same extent, and the two acids have dissociation constants of much the same value. If a solution of violuric acid contains 99 per cent. of non-ionised pseudo-acid as stated by Hantzsch, then it is calculated that the true acid is twice as strong as monochloroacetic acid.

J. J. S.

Acylation of Anilinesulphonic Acids. GEORG SCHROETER [with GEORG RÜSING] (*Ber.*, 1906, **39**, 1559—1570).—Finely-powdered dry sodium sulphanilate and acetic anhydride interact with development of heat to form sodium acetylaniline-*p*-sulphonate (Nietzki and Benckiser, *Abstr.*, 1884, 1024), which is readily soluble in water, but is only sparingly so in alcohol, and has no physiological action. The acid $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$ (Armstrong, *Proc.*, 1899, **15**, 177; Junghahn, *Abstr.*, 1900, i, 389) is obtained in slender needles on addition of concentrated hydrochloric acid to the cold concentrated aqueous solution of the sodium salt; it separates from a mixture of alcohol and ether as an oil, which solidifies to a powder containing $2\text{H}_2\text{O}$, is readily soluble in water or alcohol, but is insoluble in concentrated hydrochloric acid, and is hydrolysed only slowly when boiled with water, but more rapidly by boiling alcohol, forming sulphanilic acid and acetic acid and ethyl acetate respectively.

Acetylaniline-p-sulphonyl chloride, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{Cl}$, is formed when sodium acetyl-*p*-anilinesulphonate is ground with phosphorus pentachloride and treated with cold water; it crystallises from benzene in small needles, melts at 149° , is readily soluble in alcohol, ether, or ethyl acetate, and reacts with sodium ethoxide in alcoholic solution to form *ethyl acetylaniline-p-sulphonate*, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Et}$, which crystallises in white needles and melts at 115° . *Acetylaniline-*

p-sulphonylphenetidine, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}$, formed by the action of the sulphonyl chloride on phenetidine, crystallises from aqueous solution in glistening, white leaflets and melts at 204° .

Sodium acetylnaphthionate, $\text{C}_{12}\text{H}_{10}\text{O}_4\text{NSNa}$, prepared by treating sodium naphthionate with acetic anhydride, is obtained as a white powder, which is soluble in water, but only sparingly so in alcohol. Acetylnaphthionic acid, $\text{NHAc} \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_3\text{H} \cdot \frac{1}{2}\text{H}_2\text{O}$, crystallises in needles, is insoluble in concentrated hydrochloric acid, and when boiled with water is hydrolysed to acetic and naphthionic acids. Acetylnaphthionyl chloride, $\text{NHAc} \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_2\text{Cl}$, prepared by grinding the dry sodium salt with phosphorus pentachloride, separates from ethyl acetate in transparent crystals and decomposes, but does not melt, when heated. Ethyl acetylnaphthionate, $\text{NHAc} \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_3\text{Et}$, crystallises from benzene in white needles and melts at 148° . The anilide, $\text{NHAc} \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_2 \cdot \text{NHPh}$, crystallises from alcohol in leaflets and melts at 231° .

Sodium 5-acetylaminonaphthalene-1-sulphonate, $\text{NHAc} \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_3\text{Na}$, is formed by heating sodium 5-aminonaphthalene-1-sulphonate with acetic anhydride; when treated with phosphorus pentachloride, it yields 5-acetylaminonaphthalene-1-sulphonyl chloride,
 $\text{NHAc} \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_2\text{Cl}$.

Sodium benzoylaniline-*p*-sulphonate, $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Na}$, formed by shaking sodium sulphanilate with benzoyl chloride and sodium hydroxide in aqueous solution, crystallises in white needles, and, when ground with phosphorus pentachloride, yields benzoylaniline-*p*-sulphonyl chloride, $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{Cl}$, which crystallises in yellow needles and melts at 176° .

Sodium benzoylnaphthionate, $\text{NHBz} \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_3\text{Na}$, is formed by heating sodium naphthionate with benzoic anhydride.

Sodium benzenesulphonylaniline-*p*-sulphonate, $\text{C}_{12}\text{H}_{10}\text{O}_5\text{NS}_2\text{Na}$, is formed by shaking sodium sulphanilate with benzenesulphonyl chloride and aqueous sodium hydroxide. The acid, $\text{SO}_2\text{Ph} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$, forms an oil, which crystallises and melts at 78° . The chloride, $\text{SO}_2\text{Ph} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{Cl}$, crystallises in white needles and melts at 177° .

Sodium benzenesulphonylnaphthionate, $\text{C}_{16}\text{H}_{12}\text{O}_5\text{NS}_2\text{Na}$, prepared in the same manner from sodium naphthionate, crystallises from alcohol in leaflets. The free acid, $\text{SO}_2\text{Ph} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_3\text{H}$, crystallises in needles. The sulphonyl chloride, $\text{SO}_2\text{Ph} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_2\text{Cl}$, crystallises from benzene and melts at 171° .

Sodium acetylnaphthionate reacts with diazotised bases in aqueous solution to form diazonium salts, $\text{NHAc} \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_3 \cdot \text{N}_2 \cdot \text{Ar}$, which may be recrystallised from moderately hot water, are soluble in aqueous sodium hydroxide, give dark violet precipitates with ammonia in aqueous solution, detonate when heated on platinum, decompose and evolve nitrogen when boiled with water, and crystallise as follows.

With α -naphthylamine: crystallises in yellowish-brown, glistening, silky leaflets; with diazotised *o*- or *p*-nitroaniline: dark red, glistening needles; with diazotised *m*-nitroaniline: light yellowish-red leaflets; with diazotised benzidine: glistening, red needles.

Similar diazonium salts are obtained by the action of sodium

5-acetylaminonaphthalene-1-sulphonate on diazotised *p*-nitroaniline, crystallising in reddish-brown, and on diazotised benzidine, crystallising in yellowish-brown leaflets.

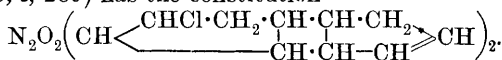
In aqueous solution, sodium benzenesulphonylaniline-*p*-sulphonate reacts with diazotised benzidine to form a yellowish-brown *diazonium* salt, $C_{36}H_{28}O_{10}N_6S_4$, which chars when heated, and gives a violet-black precipitate with ammonia; with diazotised *o*-nitroaniline to form the *diazonium* salt, $C_{18}H_{14}O_7N_4S_2$, which crystallises in orange-yellow needles and forms a red solution in aqueous sodium hydroxide; with diazotised *m*-nitroaniline to form the yellow powder, $C_{18}H_{14}O_7N_4S_2$, which dissolves to a red solution in aqueous sodium hydroxide, and with diazotised α -naphthylamine and ψ -cumidine to form similar *diazonium* salts. It couples with diazotised *p*-nitroaniline, forming the *azo*-dye, $C_{18}H_{14}O_7N_4S_2$, which crystallises in reddish-yellow needles, dissolves in aqueous sodium hydroxide or ammonia, forming a red solution, does not evolve nitrogen when boiled with water, and dyes wool yellow in an acid solution.

In aqueous solution, sodium benzenesulphonylnaphthionate reacts with diazotised benzidine to form the *diazonium* salt, $C_{44}H_{32}O_{10}N_6S_4$, which is obtained as a yellow powder, and with diazotised *m*-nitroaniline to form the yellow *diazonium* salt, $C_{22}H_{16}O_7N_4S_2$. With diazotised *p*-nitroaniline, sodium benzenesulphonylnaphthionate forms the *azo*-dye, $C_{22}H_{16}O_7N_4S_2$, which crystallises in red needles, does not evolve nitrogen when boiled with water, and dyes wool orange.

When cotton-wool is boiled with benzenesulphonylaniline-*p*-sulphonyl chloride in chloroform solution in presence of pyridine, washed, and treated with *p*-nitrophenyldiazonium acetate, the fibres are dyed yellow.

Mercerised cotton-wool is dyed orange-brown when boiled with benzenesulphonylnaphthionyl chloride in chloroform solution, washed, and treated with *p*-nitrophenyldiazonium solution. G. Y.

Dicyclopentadienes. I. HEINRICH WIELAND (*Ber.*, 1906, 39, 1492—1499).—Krämer and Spilker's dicyclopentadiene nitrosochloride (*Abstr.*, 1896, i, 289) has the constitution



When heated with diethylaniline at 140° , it is converted into the mononitrosochloride, $CH \begin{array}{c} \nwarrow CH_2 \cdot CH \cdot CH \cdot CH_2 \cdot CCl \cdot O \\ \nearrow CH \cdot CH \cdot CH \end{array} \nearrow CH \cdot NH$, which crystallises from alcohol in hard, colourless plates, melts and commences to decompose at 160° , and is readily soluble in most solvents.

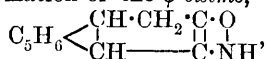
The *quinolinium chloride*, $OH \cdot N : C_{10}H_{11} \cdot C_5NH_7 \cdot Cl$, which crystallises in colourless needles and decomposes at 270° , and the *pyridinium chloride*, $OH \cdot N : C_{10}H_{11} \cdot C_5NH_5 \cdot Cl$, which melts and decomposes at 218° , and forms a *platinichloride* crystallising in stellate aggregates of orange needles and blackening at 205° , are obtained by heating Krämer and Spilker's nitrosochloride with quinoline and pyridine respectively.

When reduced with zinc dust and glacial acetic acid in methyl

alcoholic solution, the mononitrosochloride forms the *oxime* of ketodihydrodicyclopentadiene, $C_5H_6 \begin{smallmatrix} \text{CH} & \text{---} & \text{CH}_2 \\ | & & | \\ \text{CH} & \cdot & \text{C}(\text{NOH}) \end{smallmatrix} > CH_2$, which crystallises in large, fan-shaped crystals, melts at 88° , is readily soluble in most solvents, and when boiled with dilute sulphuric acid yields an aromatic oil with a nitrile-like odour.

Aminodihydrodicyclopentadiene, $C_5H_6 \begin{smallmatrix} \text{CH} & \text{---} & \text{CH}_2 \\ | & & | \\ \text{CH} & \cdot & \text{CH}(\text{NH}_2) \end{smallmatrix} > CH_2$, is formed together with the oxime by the reduction of the nitrosochloride or by reduction of the oxime with zinc dust and hydrochloric acid; the *hydrochloride* crystallises in glistening prisms and melts at 198° ; the *picrate* forms matted, yellow needles and melts and blackens at 193° .

The action of alcoholic potassium hydroxide on the mononitrosochloride leads to the formation of the *ψ-oxime*,



which melts and decomposes at 205° and is insoluble in alkali hydroxides.

Chloroaminodihydrodicyclopentadiene, $C_5H_6 \begin{smallmatrix} \text{CH} & \text{---} & \text{CH}_2 \\ | & & | \\ \text{CH} & \cdot & \text{CH}(\text{NH}_2) \end{smallmatrix} > \text{CHCl}$, is prepared by reduction of Krämer and Spilker's nitrosochloride with granulated zinc and boiling alcoholic hydrochloric acid; it is obtained as an oil with a strong, repulsive odour. The *hydrochloride*, $C_{10}H_{15}NCl_2$, crystallises in stout, glistening plates, commences to melt and decompose at 260° , and when treated with sodium nitrite and hydrochloric acid yields the corresponding volatile *alcohol*. The *platini-chloride*, $(C_{10}H_{14}NCl)_3 \cdot H_2PtCl_6$, crystallises in stellate aggregates of yellowish-brown needles and melts and decomposes at 205° ; the *picrate*, $C_{16}H_{18}O_7N_4Cl$, forms glistening, greenish-yellow needles and decomposes at 228° . G. Y.

Dipropylacetyl-*p*-phenetidine. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 163034).—*Dipropylacetyl-*p*-phenetidine*, $CHPr_2 \cdot CO \cdot NH \cdot C_6H_4 \cdot OEt$, prepared by boiling *α*-propylvaleric acid and *p*-phenetidine in a reflux apparatus, crystallises from benzene, melts at 147° , and dissolves sparingly in hot water, readily in hot alcohol or benzene. It finds therapeutic application as a substitute for antipyrine. C. H. D.

Action of Primary Amines on Aldehydes. LEOPOLD RÜGHEIMER (*Ber.*, 1906, **39**, 1653—1664).—Compounds of the type $CCl_3 \cdot CH(NH \cdot R)_2$, formed from chloral and aromatic amines, are sufficiently stable to permit of being directly nitrated. When *p*-ditoluidinetrichloroethane, $CCl_3 \cdot CH(NH \cdot C_6H_4Me)_2$, for example, is added to a mixture of anhydrous nitric acid and glacial acetic acid, it is nitrated, and, when the product is poured into water, chloral separates, whilst *m*-nitro-*p*-toluidine can also be obtained by saturating the solution with sodium carbonate. Compounds of the type $CCl_3 \cdot CH(OH) \cdot NHR$, described in the paper, do not, however, behave in an analogous manner.

The mechanism of the interaction between primary amines and aldehydes is discussed.

Chloral-o-phenylenediamine, $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, prepared by the addition of a solution of chloral in light petroleum to a solution of *o*-phenylenediamine in ether, is a colourless solid melting at about 72° . When the compound is added to sulphuric acid at -6° , the odour of chloral is perceptible. Diacetyl-*o*-phenylenediamine is formed by the action of acetic anhydride.

Chloral-p-phenylenediamine, prepared in an analogous manner, decomposes at about 80° .

Chloral-1:2:4-tolylenediamine, $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH}_2$, melts at about 86° .

Chloral-1:3:4-tolylenediamine melts at $67-68^\circ$. Its *mercuri-chloride* separates from chloroform in needles and decomposes at about 120° .

Dichloral-1:3:4-tolylenediamine, $\text{C}_6\text{H}_3\text{Me}[\text{NH} \cdot \text{CH}(\text{OH}) \cdot \text{CCl}_3]_2$, melts at $56-57^\circ$.

Chloral- α -naphthylamine, $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7$, prepared from chloral and α -naphthylamine, crystallises in needles and melts at $93-93.5^\circ$. It forms acetonephthalide when acted on by acetic anhydride.

Chloral- β -naphthylamine separates from light petroleum in needles and melts at 101° .

Chloral-aniline chloral hydrate, $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{NHPh}, \text{CCl}_3 \cdot \text{CH}(\text{OH})_2$, prepared by the addition of a solution of chloral in light petroleum to a solution of aniline in ether, separates in needles, grouped in rosettes, and melts at 56.5° .

Chloral-p-toluidine chloral hydrate,
 $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}, \text{CCl}_3 \cdot \text{CH}(\text{OH})_2$,
 melts at $58-59.5^\circ$. A. McK.

Rate of Auto-racemisation of Optically Active Ammonium Salts. EDGAR WEDEKIND (*Zeit. Elektrochem.*, 1906, 12, 330-333).—The velocity of the spontaneous change of *d*-phenylbenzylmethyl-propylammonium iodide into the racemic form in chloroform solution at 25° is measured. The reaction appears to be unimolecular, which is in accordance with the view that the change is due to the dissociation of the salt into the substituted ammonia and alkyl iodide, which subsequently recombine to the racemic form. T. E.

Chlorophenylcarbamides. RICHARD DOHT (*Monatsh.*, 1906, 27, 213-223. Compare Abstr., 1905, i, 49).—*o*-Chlorophenylcarbamide, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Cl}$, formed by the action of potassium cyanate on *o*-chloroaniline, crystallises in thin, doubly refracting, monoclinic prisms, melts at 152° (corr.), and is soluble in water, alcohol, or acetone.

m-Chlorophenylcarbamide, prepared from *m*-chloroaniline, crystallises in large, pointed, doubly refracting needles and melts at 142° (corr.).

p-Chlorophenylcarbamide is formed by the action of potassium cyanate on *p*-chloroaniline, or of 1 mol. of chlorine or of bleaching powder equivalent to 1 mol. of chlorine on phenylcarbamide in acetic

acid solution; it crystallises in doubly refracting prisms and melts at 204—207° (corr.).

2:4-Dichlorophenylcarbamide, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{Cl}_2$, is formed by the action of an excess of chlorine, or of bleaching powder equivalent to not less than 2 mols. of chlorine, on phenylcarbamide in acetic acid solution; it crystallises in sheaves of broad needles, melts at 189° (corr.), and when boiled with acetic anhydride yields 2:4-dichloroacetanilide, melting at 143°.

The action of chlorine on phenylcarbamide in hot glacial acetic acid solution leads to the formation of 2:4:6-trichloroacetanilide, ammonium chloride, and carbon dioxide. G. Y.

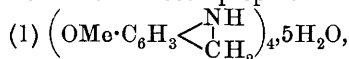
New Synthesis of Benzyleneimide. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 1272—1277).—The author has synthesised benzyleneimide by the interaction of aniline and formaldehyde in presence of tartaric or citric acid. The yellow base, to which, when

dried at 100°, the author ascribes the formula $(\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \\ | \\ \text{CH}_2 \end{smallmatrix})_4 \cdot 3\text{H}_2\text{O}$, is soluble in dilute or concentrated acetic acid and dissolves sparingly in chloroform. The addition of sodium nitrite to a solution of the imide in acetic or a mineral acid yields the corresponding isonitroso-compound, which readily forms colouring matters with alkaline β -naphthol or similar compounds. For technical purposes, it is not necessary to isolate the base in order to introduce the nitroso-compound, the original acetic acid compound being employed. The addition of excess of mercuric chloride to an acetic acid solution of the imide precipitates a yellow compound, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \\ | \\ \text{CH}_2 \end{smallmatrix} \cdot \text{H}_2\text{O} \cdot \text{HgCl}_2$.

When kept, an acetic acid solution of the isonitroso-compound deposits an orange precipitate of the nitroso-compound, $\text{NO} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NH} \\ | \\ \text{CH}_2 \end{smallmatrix}$.

Benzyleneimide can also be synthesised by first preparing anhydro-formaldehydeaniline and then heating this with tartaric and acetic acids.

The following imides have also been prepared:



from *o*-anisidine, is an amorphous powder melting at above 100°;

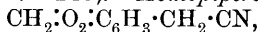
(2) $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{NH} \\ | \\ \text{CH}_2 \end{smallmatrix} \cdot 3\text{H}_2\text{O}$, from *o*-toluidine, resembles the preceding and melts at above 100°. (3) The imide from *p*-toluidine is a soft resin which solidifies on standing. T. H. P.

Constitution and Colour of Nitrophenols. GEORG VON GEORGIEVICS (*Ber.*, 1906, 39, 1536—1538. Compare Hantzsch, this vol., i, 353).—Aqueous and alcoholic solutions of picric acid darken when heated, regaining the original colour on cooling. Wool is dyed a lighter shade in a cold than in a hot picric acid bath; on prolonged boiling with water, the wool dyed in the cold darkens to the shade of that dyed in the hot bath. If picric acid is exposed to the air in a thin layer, it darkens in colour, and if treated with benzene is

separated into the ordinary yellow, soluble picric acid and a dark modification which is almost insoluble in benzene, becomes still darker above 200° , and does not melt at 230° . G. Y.

Catalytic Action of the Alkali and Alkaline-earth Salts in the Fixation of Atmospheric Oxygen by Solutions of the Polyphenols. E. FOUARD (*Compt. rend.*, 1906, 142, 796—798).—The halogen salts of the alkali and alkaline-earth metals exert a catalytic action on the absorption of oxygen by solutions of guaiacol or quinol. If to equal volumes of $2N$ solutions of the chlorides of the metals a definite quantity of a guaiacol solution is added, the time (t) required for each solution to attain a definite blue tint varies inversely with the equivalent (v) of the metal; the curve representing the relation between t and v is hyperbolic, and expressed by the equation $tv^x = \text{constant}$. The amount of oxygen absorbed in a given time by a definite quantity of quinol in the presence of equal volumes of $2N$ solutions of the metallic chlorides is greatest in the case of sodium, and then follow, in decreasing order of activity, manganese, calcium, potassium, barium, lithium, and strontium. M. A. W.

Derivatives of Catechol Methylene Ether. PAUL MEDINGER (*Monatsh.*, 1906, 27, 237—246).—*Homopiperonylnitrile*,



is formed by boiling the oxime of homopiperonaldehyde (Bouveault and Wahl, *Abstr.*, 1902, i, 682) with acetic anhydride in a reflux apparatus for thirty minutes; it is obtained as a yellow oil, which distils at 159° under 14 mm. pressure, solidifies to compact, white crystals melting at 42° , and is hydrolysed to homopiperonylic acid when boiled with alcoholic potassium hydroxide. The *acetyl* derivative of homopiperonaldoxime, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_8\cdot\text{CH}_2\cdot\text{CH}:\text{N}\cdot\text{OAc}$, is formed together with the nitrile when the oxime is boiled with acetic anhydride for fifteen minutes; it distils at 177° under 14 mm. pressure, solidifies to white crystals melting at 96° , and on prolonged heating in a reflux apparatus decomposes, forming acetic acid and the nitrile.

Homopiperonylamine, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_8\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$, prepared by reducing the oxime of homopiperonaldehyde with sodium and alcohol, is obtained as a colourless oil, which boils at 145° under 17 mm. pressure; the colourless, crystalline *hydrochloride*, $\text{C}_9\text{H}_{11}\text{O}_2\text{N}\cdot\text{HCl}$, melts at 197° and is readily soluble in water.

Homopiperonyl alcohol, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_8\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, formed by the action of silver nitrite on the hydrochloride of the amine in aqueous solution, is obtained as an almost colourless, strongly refracting oil with a pleasant aromatic odour, which boils at 164° under 18 mm. pressure. G. Y.

***o-o*-Dihydroxydiphenyl Sulphide.** FERDINAND MAUTHNER (*Ber.*, 1906, 39, 1347—1351).—Thioguaiacol was prepared from *o*-anisidine by Leuckart's diazo-reaction, whilst *thioguaiacol xanthate* was obtained as a by-product; the latter separates from alcohol in colourless leaflets and melts at 123° . Thioguaiacol was converted into its sodium salt, which was condensed with *o*-iodoanisole in the presence of copper as a catalyst

to form *o-o-dimethoxydiphenyl sulphide*, $C_{14}H_{14}O_2S$, which separates from alcohol in colourless leaflets, melts at 73° , and boils at $252-253^\circ$ under 10 mm. pressure. Its solution in concentrated sulphuric acid is blue, and becomes colourless on the addition of water.

o-o-Dimethoxydiphenylsulphone, prepared by the oxidation of the sulphide by potassium permanganate, crystallises from benzene in colourless needles and melts at $157-158^\circ$. Its solution in concentrated sulphuric acid becomes blue on warming, but loses this tint when diluted with water.

When *o-o*-dimethoxydiphenyl sulphide in xylene solution is warmed for two hours with aluminium chloride, *o-o-dihydroxydiphenyl sulphide*, $C_{12}H_{10}O_2S$, may be isolated from the product; it separates from benzene in colourless needles and melts at 142° . Its solution in sulphuric acid is bright green, but this tint disappears when the solution is diluted. In aqueous solution it gives a green coloration with ferric chloride. Its *acetyl* derivative separates from alcohol in colourless needles and melts at $95-96^\circ$. *Acetyl o-o-dihydroxydiphenylsulphone*, $C_{16}H_{14}O_6S$, prepared by oxidising *o-o*-diacetyldihydroxydiphenyl sulphide in glacial acetic acid solution with potassium permanganate, separates from alcohol in colourless needles and melts indefinitely at $147-148^\circ$. It forms a blue solution with concentrated sulphuric acid. When treated with sodium hydroxide and the solution then acidified, the acetyl compound forms *o-o-dihydroxydiphenylsulphone*, $C_{12}H_{10}O_4S$, which separates from benzene in colourless needles and melts at $164-165^\circ$. Its solution in sulphuric acid is blue, and becomes colourless on dilution with water.

A. McK.

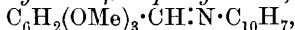
Conversion of Morphenol into Trihydroxyphenanthrene.

EDUARD VONGERICHTEN and O. DITTMER (*Ber.*, 1906, **39**, 1718—1722). —*3:4:5-Trihydroxyphenanthrene*, $C_{14}H_{10}O_3$, is obtained when morphenol is heated with potassium hydroxide at 250° ; after purification, it separates from water in glassy leaflets, softens at 120° , and melts at 148° . When heated in methyl-alcoholic solution with methyl iodide and sodium methoxide, it yields *3:4:5-trimethoxyphenanthrene*, $C_{17}H_{16}O_3$, which melts at 90° . The *picrate* melts at 166° . The triacetyl derivative, which could not be obtained in the crystalline state, is readily oxidised by chromic and glacial acetic acids to a quinone which dissolves in alcoholic soda to a red solution, quickly changing to violet, and forms with *o*-tolylenediamine a yellow, crystalline azine. The compound of the quinone with sodium hydrogen sulphite is decomposed by sulphuric acid, yielding a quinone which dissolves in alcoholic soda to an intensely violet solution.

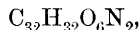
C. S.

Condensation Products of Asaryl Aldehyde. RUDOLF

FABINYI and TIBOR SZÉKI (*Ber.*, 1906, **39**, 1211—1218. Compare Butleroff and Rizza, *Abstr.*, 1885, 669; Gattermann and Eggers, *Abstr.*, 1899, i, 347). —*2:4:5-Trimethoxybenzylidene semicarbazide*, $C_6H_2(OMe)_3 \cdot CH:N \cdot NH \cdot CO \cdot NH_2$, crystallises from alcohol in small, white needles and melts at $205-206^\circ$.

2 : 4 : 5-Trimethoxybenzylidene-β-naphthylamine,

crystallises from alcohol in yellow leaflets and melts at 134°; the *hydrochloride*, $\text{C}_{20}\text{H}_{19}\text{O}_3\text{N} \cdot \text{HCl}$, forms glistening, red, rhombic crystals with blue lustre and dissolves in water to a yellow solution.

2 : 2' : 4 : 4' : 5 : 5'-Hexamethoxydibenzylidenebenzidine,

crystallises in slender needles and is readily soluble in chloroform or benzene, but only sparingly so in alcohol or ether; the *hydrochloride*, $\text{C}_{32}\text{H}_{32}\text{O}_6\text{N}_2 \cdot 2\text{HCl}$, forms slender, red, microscopic needles.

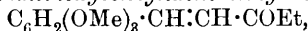
1-Phenyl-4(2' : 4' : 5')-trimethoxybenzylidene-3-methyl-5-pyrazolone, $\text{NPh} \cdot \text{CO} \begin{array}{l} | \\ \text{N}=\text{CMe} \end{array} > \text{C} : \text{CH} \cdot \text{C}_6\text{H}_2(\text{OMe})_3$, formed by the action of the aldehyde on phenylmethylpyrazolone in alcoholic solution at the ordinary temperature, crystallises in long, slender, glistening, orange-red needles and melts at 230°.

2 : 4 : 5-Trimethoxybenzylideneacetone,

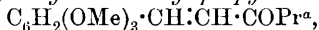
formed by the interaction of asaryl aldehyde and acetone in presence of sodium hydroxide in warm alcoholic solution, crystallises in delicate, orange-yellow leaflets, melts at 173°, and gives with concentrated sulphuric acid a cherry-red, and with bromine in chloroform solution a greenish-blue, coloration, becoming yellow on addition of an excess of bromine. With bromine in carbon disulphide solution, it forms a yellow, crystalline *dibromide* (?). The *di-iodide*,



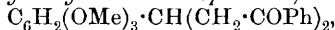
formed by the action of iodine on trimethoxybenzylideneacetone in warm alcoholic solution, separates in glistening, metallic, dark bluish-green, woolly crystals, and is decomposed into iodine and trimethoxybenzylideneacetone when boiled with water. The *oxonium hydrochloride*, $\text{C}_{13}\text{H}_{16}\text{O}_4 \cdot \text{HCl}$, is formed by the action of hydrogen chloride on trimethoxybenzylideneacetone in absolute alcoholic solution; it separates in bluish-green, woolly crystals with metallic lustre, and is unstable. *2 : 4 : 5-Trimethoxybenzylidenemethyl ethyl ketone*,



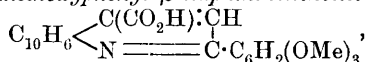
formed by the condensation of trimethoxybenzaldehyde with methyl ethyl ketone in presence of sodium hydroxide in aqueous-alcoholic solution, separates in light yellow crystals, melts at 155°, and gives an intense red coloration with bromine in chloroform solution.

2 : 4 : 5-Trimethoxybenzylidenemethyl propyl ketone,

crystallises in yellow needles and melts at 87°.

2 : 4 : 5-Trimethoxybenzylidenediacetophenone,

crystallises from alcohol in slender, white needles and melts at 119—120°. The oxime, $\text{C}_{26}\text{H}_{28}\text{O}_5\text{N}_2$, forms white needles and melts at 167—168°.

2(2' : 4' : 5')-Trimethoxyphenyl-β-naphthacinchonic acid,

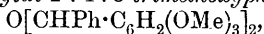
is prepared by heating 2 : 4 : 5-trimethoxybenzaldehyde with β-naphthylamine and pyruvic acid in absolute alcoholic solution in a

reflux apparatus; it crystallises in matted, slender, yellow needles, melts at 258° , and is insoluble in the ordinary solvents.

2 : 4 : 5-Trimethoxy- α -phenylcinnamionitrile,
 $\text{C}_6\text{H}_2(\text{OMe})_3 \cdot \text{CH} : \text{CPh} \cdot \text{CN}$,

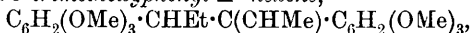
formed by condensation of trimethoxybenzaldehyde with benzyl cyanide, crystallises in yellowish-green needles and melts at $147-148^{\circ}$. G. Y.

Action of Magnesium Organic Compounds on Asaryl Aldehyde. RUDOLF FABINYI and TIBOR SZÉKI (*Ber.*, 1906, 39, 1218—1222).—*Diphenyl-di-2 : 4 : 5-trimethoxyphenylmethyl ether*,

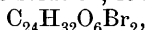


is formed by the action of magnesium phenyl iodide on asaryl aldehyde in benzene-ethereal solution; it crystallises in delicate, colourless leaflets or needles, melts at 210° , is readily soluble in hot benzene, glacial acetic acid, or chloroform, and gives with concentrated sulphuric acid an intense red and with concentrated hydrochloric acid a red coloration changing to blue.

$\gamma\delta$ -Di-2 : 4 : 5-trimethoxyphenyl- Δ^{β} -hexene,



is formed by the action of magnesium ethyl iodide on asaryl aldehyde in benzene-ethereal solution; it crystallises from alcohol in small, white leaflets, melts at 96° , dissolves in concentrated sulphuric acid forming a yellowish-red solution, and gives with concentrated hydrochloric acid a red coloration changing to blue. When heated with bromine in carbon disulphide solution, it forms the *dibromide*,



which crystallises in small, white needles, gradually becomes grey, and melts and decomposes at $104-106^{\circ}$.

Di-2 : 4 : 5-trimethoxy- α -phenyl ethyl ether, $\text{O}[\text{CHMe} \cdot \text{C}_6\text{H}_2(\text{OMe})_3]_2$, formed by the action of magnesium methyl iodide on asaryl aldehyde, crystallises from alcohol and melts at 111.5° . G. Y.

Monohalogen Derivatives of Triphenylcarbinol Chloride [Triphenylchloromethane]. LEE H. CONE and C. P. LONG (*J. Amer. Chem. Soc.*, 1906, 28, 518—524).—*p*-Bromotriphenylchloromethane (Gomberg, *Abstr.*, 1904, i, 489) can be prepared by the action of hydrogen chloride on the carbinol obtained by the reaction between magnesium phenyl bromide and methyl *p*-bromobenzoate or *p*-bromobenzophenone.

p-Bromotriphenylcarbinol, $\text{C}_6\text{H}_4\text{Br} \cdot \text{CPh}_2 \cdot \text{OH}$, obtained by heating *p*-bromotriphenylchloromethane with a mixture of glacial acetic and sulphuric acids, forms colourless crystals and melts at 74° . *p*-Bromotriphenylmethyl peroxide, $\text{O}_2(\text{CPh}_2 \cdot \text{C}_6\text{H}_4\text{Br})_2$, crystallises from ether or light petroleum and melts at $171.5-173.5^{\circ}$. *p*-Bromotriphenylmethylamine, $\text{C}_6\text{H}_4\text{Br} \cdot \text{CPh}_2 \cdot \text{NH}_2$, is a crystalline substance which melts at $108.5-109^{\circ}$. *p*-Bromotriphenylmethylaniline melts at 148° .

p-Bromobenzophenone can be obtained in nearly quantitative yield by the action of benzoyl chloride on bromobenzene in presence of aluminium chloride. On attempting to prepare *p*-bromotriphenylchloromethane by the action of benzene on the product of the reaction between phosphorus pentachloride and *p*-bromobenzophenone, a

mixture of *p*-bromo- and *p*-chloro-triphenylchloromethanes was obtained. This result was found to be due to the fact that the product obtained by the action of phosphorus pentachloride on *p*-bromobenzophenone was not the dichloride expected but a mixture of *p*-chloro- and *p*-bromo-benzophenones.

m-Bromotriphenylchloromethane, prepared by Grignard's reaction from ethyl *m*-bromobenzoate, melts at 67°. E. G.

Hydrogenisation of Cholesterol. OTTO DIELS and EMIL ABDERHALDEN (*Ber.*, 1906, 39, 1371—1373).—A reply to Neuberg (this vol., i, 356).

α -Cholesterol (this vol., i, 272) cannot be identical with coprosterol (Bondzynski, *Abstr.*, 1896, ii, 319), as the two compounds differ in melting point, solubility, and in the characteristics of the benzoyl derivatives. C. S.

A Simple General Method for the Synthesis of α -Amino-acids. NICOLAI ZELINSKY and GEORGE STADNIKOFF (*Ber.*, 1906, 39, 1722—1732).—The nitriles of α -amino-acids are formed when equal molecular quantities of potassium cyanide and ammonium chloride react in aqueous or aqueous-alcoholic solution with aldehydes or ketones of the aliphatic, aromatic, or hydroaromatic series (compare Ljubavin, *Abstr.*, 1883, 178; Eschweiler, *Abstr.*, 1894, i, 267; Curtius and Jay, *ibid.*, i, 162; Gulewitsch, *Abstr.*, 1900, i, 476). The probable course of the reaction is indicated in the scheme: $\text{KCN} + \text{H}_2\text{O} \rightleftharpoons \text{KOH} + \text{HCN}$; $\text{R}\cdot\text{CO}\cdot\text{R}(\text{or H}) + \text{HCN} = \text{R}(\text{or H})\text{CR}(\text{OH})\cdot\text{CN}$; $\text{NH}_4\text{Cl} + \text{KOH} = \text{NH}_3 + \text{KCl} + \text{H}_2\text{O}$; $\text{R}(\text{or H})\text{CR}(\text{OH})\cdot\text{CN} + \text{NH}_3 = \text{H}_2\text{O} + \text{R}(\text{or H})\text{CR}(\text{NH}_2)\cdot\text{CN}$.

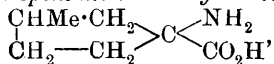
The nitrile of α -aminophenylacetic acid was obtained from benzaldehyde in 60 per cent. yield, and α -aminoisobutyric acid from acetone in 72.8 per cent. yield.

The following new compounds are described:

α -Aminocyclohexylacetic acid, $\text{CH}_2\left\langle\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix}\right\rangle\text{CH}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$,

obtained from hexahydrobenzaldehyde in 80 per cent. yield, separates from water in crystalline nodules and melts and decomposes at 297°. The *picrate* crystallises in yellow prisms and melts and decomposes at 186—187°.

3-Amino-1-methylcyclopentane-3-carboxylic acid,



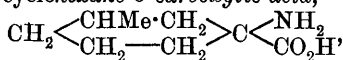
obtained from 1-methylcyclopentane-3-one in 59 per cent. yield, is very soluble in water, and melts and decomposes at 299—300°. In aqueous solution, the acid does not exhibit optical activity, although it is obtained from an active ketone (*Abstr.*, 1902, i, 597). The *copper* salt forms blue anhydrous crystals.

1-Aminocyclohexane-1-carboxylic acid, $\text{CH}_2\left\langle\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix}\right\rangle\text{C}\left\langle\begin{smallmatrix} \text{NH}_2 \\ \text{CO}_2\text{H} \end{smallmatrix}\right\rangle$,

obtained from cyclohexanone in 93 per cent. yield, separates from water in octahedral crystals or in long prisms, and melts and decom-

poses at 334—335°. The *hydrochloride* softens at 280° and melts and decomposes at 310°. The *copper* salt forms dark blue crystals containing 1H₂O. The *picrate* melts and decomposes at 209—210°.

3-Amino-1-methylcyclohexane-3-carboxylic acid,



obtained from 1-methylcyclohexane-3-one in 52 per cent. yield, separates from water in small plates containing 1H₂O, and when anhydrous melts and decomposes at 330°. In acetic acid solution, it is optically inactive, although derived from an active ketone.

1-Aminocycloheptane-1-carboxylic acid, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{C} \begin{array}{c} \text{NH}_2 \\ \text{CO}_2\text{H} \end{array}$,

obtained from suberone, separates from water in aggregates of glistening prisms containing 1 mol. H₂O. The anhydrous acid melts and decomposes at 306—307°, the *picrate* at 215—216°. The *copper* salt exists in three forms: bluish-violet plates containing 1 mol. H₂O, small, sky-blue anhydrous crystals, and reddish-violet needles. C. S.

Phenylation in the Presence of Copper as a Catalyst. IRMA GOLDBERG (*Ber.*, 1906, 39, 1691—1692).—A theoretical yield of phenylanthranilic acid may be obtained by interaction of anthranilic acid and bromobenzene in presence of a trace of copper. *p*-Bromonitrobenzene and anthranilic acid yield similarly 4-nitrophenylanthranilic acid.

The action may also be extended to acid amides. Benzamide reacts with bromobenzene in the presence of copper to form benzanilide. Similarly, salicylanilide may be prepared from salicylamide.

A. McK.

Action of Ammonium Cyanide on Ketones of the Series CO(C_nH_{2n-7})(C_nH_{2n+1}). J. JAWELOFF (*Ber.*, 1906, 39, 1195—1200. Compare this vol., i, 409).—The action of ammonium cyanide on ketones of the series CO(C_nH_{2n-7})(C_nH_{2n+1}) leads to the formation of amino-nitriles and of amino-acids; the yields are diminished by the proximity of an aryl group to the carbonyl, and by the presence of *o*-methyl groups.

α-Amino-*α*-phenylpropionitrile hydrochloride is formed in a yield of 47 per cent., together with *α*-amino-*α*-phenylpropionic acid in a yield of 2 per cent. of the theoretical, by the action of ammonium cyanide on phenyl methyl ketone at 80° under pressure. The amino-nitrile hydrochloride, CN·CMePh·NH₂·HCl, forms small, yellow needles, melts at 96—97°, and is readily soluble in water or absolute alcohol, but is insoluble in ether, benzene, or carbon disulphide; the aqueous solution is acid to litmus, but does not change the colour of congo red. When slowly evaporated in absolute alcoholic solution, the aminonitrile hydrochloride yields ammonium chloride, and on recrystallisation from water it is decomposed, forming acetophenone. It is oxidised to benzoic acid by dilute alkaline permanganate solution, and on reduction with sodium and alcohol yields ammonia and *α*-phenylethylamine. *α*-Amino-*α*-phenylpropionitrile is a dark oil, which boils and partially

decomposes at 101—104° under 12·5 mm. pressure. *α-Amino-α-phenylpropionamide hydrochloride*, $\text{NH}_2 \cdot \text{CO} \cdot \text{CMePh} \cdot \text{NH}_2 \cdot \text{HCl}$, crystallises in large, colourless prisms, melts above 250°, and is readily soluble in water.

α-Amino-α-p-tolylpropionitrile hydrochloride,
 $\text{CN} \cdot \text{CMe}(\text{C}_7\text{H}_7) \cdot \text{NH}_2 \cdot \text{HCl}$,

is formed from *p*-tolyl methyl ketone in a yield of 42 per cent. of the theoretical; it crystallises in small, slightly yellow needles and melts at 104—105°. *α-Amino-α-p-tolylpropionic acid*, $\text{NH}_2 \cdot \text{CMe}(\text{C}_7\text{H}_7) \cdot \text{CO}_2\text{H}$, formed together with the amino-nitrile, crystallises from water in sheaves of long, white, silky needles, sublimes but does not melt, and forms an insoluble copper salt.

α-Amino-α-3:4-xylylpropionitrile hydrochloride,
 $\text{CN} \cdot \text{CMe}(\text{C}_6\text{H}_3\text{Me}_2) \cdot \text{NH}_2 \cdot \text{HCl}$,

which crystallises in yellow needles and melts at 103—104°, and *α-amino-α-3:4-xylylpropionic acid*, $\text{NH}_2 \cdot \text{CMe}(\text{C}_6\text{H}_3\text{Me}_2) \cdot \text{CO}_2\text{H}$, crystallising in long, white needles, are formed together from 3:4-xylyl methyl ketone in yields of 38 per cent. and 11 per cent. of the theoretical respectively.

α-Amino-α-2:4-xylylpropionitrile hydrochloride, $\text{C}_{11}\text{H}_{14}\text{N}_2 \cdot \text{HCl}$, which crystallises in yellow needles and melts at 97—98°, and the corresponding *amino-acid*, $\text{C}_{11}\text{H}_{15}\text{O}_2\text{N}$, crystallising in small plates, are formed together from 2:4-xylyl methyl ketone in yields of 13 per cent. and 8 per cent. of the theoretical respectively.

α-Amino-α-2:5-xylylpropionitrile hydrochloride, melting at 101—102°, and the corresponding *amino-acid*, crystallising in small plates, are formed from 2:5-xylyl methyl ketone in yields of 12 per cent. and 8 per cent. of the theoretical respectively.

α-Amino-α-phenylbutyronitrile hydrochloride, $\text{CN} \cdot \text{CEtPh} \cdot \text{NH}_2 \cdot \text{HCl}$, is obtained from phenyl ethyl ketone in a yield of 42 per cent. of the theoretical; it crystallises from water or alcohol in small, yellow needles and melts at 118—119°. The corresponding *amino-acid*, which is obtained in a yield of 5 per cent. of the theoretical, crystallises in small, colourless prisms.

The interaction of benzylacetone and ammonium cyanide leads to the formation of *α-amino-β-benzylisobutyronitrile hydrochloride*, $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{CMe}(\text{CN}) \cdot \text{NH}_2 \cdot \text{HCl}$, which is obtained in a yield of 66 per cent., together with *α-amino-β-benzylisobutyric acid*, which is obtained in a yield of 6 per cent. of the theoretical and crystallises in short, white needles. The amino-nitrile hydrochloride crystallises in colourless, greasy prisms, or from alcohol or water in colourless plates, and melts and decomposes at 120—122·5°. G. Y.

Reaction between Unsaturated Compounds and Organic Magnesium Compounds. VIII. Reactions with $\alpha\beta$ -Unsaturated Nitriles. ELMER P. KOHLER (*Amer. Chem. J.*, 1906, 35, 386—404. Compare Abstr., this vol., i, 96, and previous abstracts).—When *α*-phenylcinnamonitrile is added gradually to a boiling solution of magnesium ethyl bromide and the resulting magnesium compound is treated with ice-water and hydrochloric acid, two racemic modifications of *αβ*-diphenylvaleronitrile, $\text{CHPhEt} \cdot \text{CHPh} \cdot \text{CN}$, are produced, one of

which forms small, lustrous crystals, melts at 115° , and is readily soluble in acetone or boiling alcohol, and moderately so in ether, whilst the other is obtained as a colourless oil. On hydrolysing these nitriles by heating them with strong hydrochloric acid at 180° for four hours, a mixture of $\alpha\beta$ -diphenylvaleric acids, $\text{CHPhEt}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, is produced in each case. One of these acids crystallises in small, lustrous plates, melts at 178° , and is moderately soluble in ether, and slightly so in light petroleum; the other acid forms clusters of crystals, melts at 152 — 153° , and is readily soluble in alcohol or ether, and sparingly so in light petroleum. Each of these acids, when heated with concentrated hydrochloric acid at 180° for twenty-four hours, yields a mixture of the two forms.

$\alpha\beta$ -Diphenyl- α -ethylvaleronitrile, $\text{CHPhEt}\cdot\text{CPhEt}\cdot\text{CN}$, obtained by the action of ethyl iodide on the magnesium derivative, crystallises in large, tabular plates, melts at 105° , and is readily soluble in acetone, alcohol, ether, or chloroform. Attempts to hydrolyse this substance were unsuccessful. On reduction with sodium and boiling amyl alcohol, $\gamma\delta$ -diphenylhexane is produced which melts at 92° , boils at 175° under 20 mm. pressure, and is readily soluble in organic solvents.

$\alpha\beta$ -Diphenyl- α -methylvaleronitrile crystallises in prisms, melts at 99° , is readily soluble in alcohol or ether, and cannot be hydrolysed.

$\alpha\beta$ -Diphenyl- α -benzylvaleronitrile, $\text{CHPhEt}\cdot\text{CPh}(\text{C}_7\text{H}_7)\cdot\text{CN}$, crystallises from benzene in needles containing 1 mol. of the solvent, which it loses slowly at the ordinary temperature; it melts at 140° , and is readily soluble in benzene, acetone, or hot alcohol.

Although all these alkyl derivatives should be capable of existing in two inactive modifications, only one substance was obtained in each case. It is evident, therefore, that only one magnesium compound is formed by the union of phenylcinnamonitrile with magnesium ethyl bromide, and that the two stereoisomeric diphenylvaleronitriles are produced by the decomposition of this substance with water.

α -Benzoyl- $\alpha\beta$ -diphenylvaleronitrile, $\text{CHPhEt}\cdot\text{CPhBz}\cdot\text{CN}$ or $\text{CHPhEt}\cdot\text{CPh}\cdot\text{C}\cdot\text{NBz}$,

obtained by the action of benzoyl chloride on the magnesium derivative, crystallises from alcohol in large needles, melts at 137° , is readily soluble in chloroform, acetone, or hot alcohol, moderately so in cold alcohol or ether, and is easily hydrolysed with formation of benzoic acid and the solid diphenylvaleronitrile.

α -Cyano- $\alpha\beta$ -diphenylvaleric acid, $\text{CHPhEt}\cdot\text{CPh}(\text{CN})\cdot\text{CO}_2\text{H}$ or $\text{CHPhEt}\cdot\text{CPh}\cdot\text{C}\cdot\text{N}\cdot\text{CO}_2\text{H}$,

obtained by the decomposition of the product of the action of carbon dioxide on the magnesium derivative, is an oil which is fairly stable at low temperatures, but slowly evolves carbon dioxide at the ordinary temperature, and is instantly decomposed by boiling water; the salts are less stable than the acid itself.

Both modifications of diphenylvaleronitrile react with magnesium methyl iodide with the formation, in each case, of two stereoisomeric forms of $\gamma\delta$ -diphenylhexane- β -one, $\text{CHPhEt}\cdot\text{CHPh}\cdot\text{COMe}$. One of these forms crystallises in stout needles, melts at 116° , and is readily soluble in ether or acetone, and moderately so in cold alcohol. The other form crystallises from light petroleum and melts at 56° .

By the action of magnesium phenyl bromide on the two modifications of diphenylvaleronitrile, two forms of $\alpha\beta$ -diphenylvalerophenone, $\text{CHPhEt}\cdot\text{CHPh}\cdot\text{COPh}$, are obtained, one of which crystallises in needles, melts at 170° , and dissolves readily in acetone or chloroform; the other form crystallises in plates, melts at 92° , and is easily soluble in alcohol or ether.

Magnesium phenyl bromide reacts with phenylcinnamonitrile with formation of triphenylpropionitrile and benzyldenedeoxybenzoin. *Triphenylpropionitrile*, $\text{CHPh}_2\cdot\text{CHPh}\cdot\text{CN}$, crystallises in plates, melts at 102° , and is readily soluble in alcohol or ether. *Triphenylpropionamide*, $\text{CHPh}_2\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}_2$, obtained by heating the nitrile at 160° for four hours with concentrated hydrochloric acid, crystallises in needles, melts at 213° , is readily soluble in alcohol, moderately so in ether, and slightly so in boiling water; it is easily hydrolysed by strong hydrochloric acid at 200° with formation of triphenylpropionic acid. *Triphenylethylpropionitrile*, $\text{CHPh}_2\cdot\text{CPhEt}\cdot\text{CN}$, obtained together with benzyldenedeoxybenzoin by the action of ethyl iodide on a solution of the magnesium derivative, crystallises in needles, melts at 134° , dissolves readily in alcohol or ether, and undergoes no change when heated to 200° with concentrated hydrochloric acid.

By the interaction of cinnamonitrile with magnesium methyl iodide and with magnesium phenyl bromide, products are obtained which yield dibenzyldienacetone and benzyldieneacetophenone respectively. β -Phenylcinnamonitrile reacts similarly with magnesium phenyl bromide with production of β -phenylbenzyldieneacetophenone.

E. G.

Stereoisomeric Cinnamic Acids. EMIL ERLÉNMEYER, jun., and C. BARKOW (*Ber.*, 1906, **39**, 1570—1585. Compare Erlenmeyer, jun., *Abstr.*, 1905, i, 892).—The brucine salt melting at 135° is formed by the action of brucine on cinnamic acid from storax in absolute alcoholic solution; it crystallises in monoclinic plates [$a:b:c = 1.2039:1:0.7770$; $\beta = 77^\circ 39'$], dissolves in 16.44 parts of 50 per cent. ether-alcohol, and has $[\alpha]_D - 5^\circ$ in a 0.5 per cent., $[\alpha]_D \pm 0^\circ$ in a 1 per cent., or $[\alpha]_D + 12.5^\circ$ in a 10 per cent. solution in absolute alcohol. The brucine salt melting at 113° is formed by the action of brucine on cinnamic acid from storax in 50 per cent. alcoholic solution; it crystallises in monoclinic plates [$a:b:c = 2.3026:1:1.4989$; $\beta = 80^\circ 45'$], and when dried loses $\text{C}_2\text{H}_6\text{O}$ and commences to melt at 113° . It dissolves in 8.23 parts of 50 per cent. ether-alcohol, and has, when dried, $[\alpha]_D - 16.67^\circ$ in a 1 per cent., or, when containing $\text{C}_2\text{H}_6\text{O}$, $[\alpha]_D - 12.5^\circ$ in a 1 per cent., or $[\alpha]_D + 3.33^\circ$ in a 10 per cent. solution in absolute alcohol. In one experiment, when heated with alcohol, this salt was converted into that melting at 135° .

The brucine salt melting at 107° is the racemic compound of the salts melting at 135° and 113° , into which it is resolved by recrystallisation from a mixture of alcohol and ether; it dissolves in 6.92 parts of 50 per cent. ether-alcohol, and has $[\alpha]_D - 16.7^\circ$ in a 0.5 per cent. or $[\alpha]_D \pm 0^\circ$ in a 5 per cent. solution in absolute alcohol.

α -Cinnamic acid obtained from the brucine salt melting at 135° is identical with the acid from storax; it crystallises in monoclinic plates

[$\alpha:b:c = 0.8648:1:0.3142$; $\beta = 82^\circ 52'$], melts at $134-135^\circ$, dissolves in 19.8 parts of 75 per cent. alcohol, and is converted into β -cinnamic acid when heated above its melting point, or dissolved in a small quantity of ether and precipitated by addition of light petroleum, or recrystallised from 75 per cent. alcohol.

β -Cinnamic acid is obtained from Honduras balsam or from the brucine salt melting at 113° ; it crystallises in monoclinic plates [$\alpha:b:c = 3.8855:1:3.0240$; $\beta = 89^\circ 12'$], melts at 133° , dissolves in 13.12 parts of 75 per cent. alcohol, and is converted into the α -acid by repeated recrystallisation from ether, or on recrystallisation from absolute alcohol.

The acid obtained from the brucine salt melting at 107° crystallises from ether in large, thin leaflets, dissolves in 18.02 parts of 75 per cent. alcohol, and when freshly prepared can be reconverted into the brucine salt melting at 107° .

Synthetical cinnamic acid dissolves in 15.97 parts of 75 per cent. alcohol; it yields β -cinnamic acid under the same conditions as does the acid from storax, but in smaller crystals. If the synthetical acid is dissolved in hot 75 per cent. alcohol and cooled, β -cinnamic acid crystallises out together with a small amount of the α -acid, into which it changes entirely if left in contact with the solution. But if the β -acid is filtered off, the mother liquor evaporated to dryness, and the residue again recrystallised from 75 per cent. alcohol, a further amount of β -acid is obtained, which changes into the α -acid only extremely slowly.

Whilst in absolute alcoholic solution α -cinnamic acid forms the brucine salt melting at 135° quantitatively, the synthetical acid yields only half of the theoretical amount of this salt, but in 50 per cent. alcoholic solution it forms the salt melting at 113° quantitatively.

The acid obtained from storax after treatment with boiling sodium hydroxide dissolves in 15.01 parts of 75 per cent. alcohol.

Six cinnamic acids differing in crystallographical as also in other properties are now known: Erlenmeyer, sen.'s, *isocinnamic acid*, melting at $37-38^\circ$; *allocinnamic acid*, melting at 68° ; Liebermann's *isocinnamic acid*, melting at 59° ; triclinic cinnamic acid, melting at 80° ; α -cinnamic acid from storax, melting at $134-135^\circ$; and β -cinnamic acid from storax, melting at $132-133^\circ$. To these must be added *isocinnamic acid* from the most soluble brucine salt, which differs from Liebermann's acid only slightly in its crystalline form, and the synthetical acid, which differs from the storax acid in its manner of crystallisation and in the formation of the brucine salt. G. Y.

Preparation of Glycidic Esters and Aldehydes in the Hexahydroaromatic Series. GEORGES DARZENS and P. LEFÉBURE (*Compt. rend.*, 1906, 142, 714-715. Compare Abstr., 1905, i, 116; this vol., i, 62, 137).—*cyclo*Hexanone and its three methyl homologues (Sabatier and Senderens, Abstr., 1904, i, 156; 1905, i, 275) condense with ethyl chloroacetate to form $\beta\beta$ -substituted glycidic esters, which on distillation yield the corresponding hexahydrobenzaldehyde. The

compound $\text{C}_6\text{H}_{10} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$ is a viscous, colourless liquid which boils

at 128—129° under 17 mm. pressure, has an extremely disagreeable odour of rotten fruits and of scatole, and yields hexahydrobenzaldehyde (compare Bouveault, Abstr., 1904, i, 61; 1905, i, 116) on distillation under a pressure of 30 mm. The compounds obtained by condensing ethyl chloroacetate and *o*-, *m*-, or *p*-methylcyclohexanone boil at 129—131° under 15 mm. pressure, 140—143° under 20 mm. pressure, or 133° under 18 mm. pressure respectively; they are all characterised by their extremely disagreeable odour, and yield the corresponding methylhexahydrobenzaldehyde on distillation; *hexahydro-o-tolualdehyde* boils at 61—62° under 15 mm. pressure, has a strong odour of camphor, and forms a semicarbazone which melts at 137—138°; *hexahydro-m-tolualdehyde* (compare Tschitschibabin, Abstr., 1904, i, 421) boils at 60—61° under 15 mm. pressure, and *hexahydro-p-tolualdehyde* is a liquid with a characteristic aromatic odour, which boils at 64—65° under 16 mm. pressure and forms a semicarbazone which melts at 168—169°.

M. A. W.

Substitution of the Acetyl by the Methyl Group by means of Diazomethane. JOSEF HERZIG and J. TICHATSCHEK (*Ber.*, 1906, 39, 1557—1559. Compare this vol., i, 173).—Acetanilide and phenacetin do not react with diazomethane. On treatment with diazomethane and hydrolysis of the product with potassium hydroxide, *p*-acetoxybenzoic and *m*-acetoxybenzoic acids yield acids containing 73·4 per cent. and 88·6 per cent. of the corresponding methoxybenzoic acids respectively, whilst *p*-hydroxybenzoic acid yields pure anisic acid. Under similar conditions, salol forms the methyl ether quantitatively, but salicylic acid yields a product containing only 1·27 per cent. of the methyl ether, and the acetyl groups of acetylsalicylic acid and acetylsalol remain unchanged.

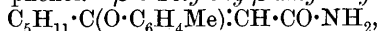
G. Y.

Synthesis of α -Amino-acids. FRANZ KNOOP and HANS HOESSLI (*Ber.*, 1906, 39, 1477—1480. Compare Knoop, Abstr., 1905, ii, 46).—Fittig and Petkow's α -keto- γ -phenylbutyric acid (Abstr., 1898, i, 196) yields an *oxime*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{C}(\text{NOH})\cdot\text{CO}_2\text{H}$, which crystallises in colourless needles, melts at 165°, and dissolves readily in most organic solvents with the exception of light petroleum. *α -Amino- γ -phenylbutyric acid*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$, is obtained when the oxime is reduced with sodium amalgam and water, care being taken to neutralise the free alkali from time to time with hydrochloric acid. It crystallises from water in colourless plates or needles, and melts and decomposes at 293—295° when quickly heated. It is tasteless, dissolves sparingly in cold water, and is insoluble in all organic solvents with the exception of ethyl alcohol. The aqueous solution does not dissolve cupric oxide or carbonate. Better yields are obtained when the reduction is accomplished by means of aluminium amalgam and moist ether. The same method of reduction is used with advantage in the preparation of phenylalanine.

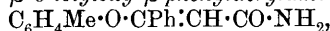
The constitution of α -keto- γ -phenylbutyric acid has been confirmed by its quantitative oxidation to β -phenylpropionic acid by means of hydrogen peroxide. Hence the amino-acid described by Fischer and

Schmitz (this vol., i, 182) under the same name must have a different constitution. J. J. S.

Condensation of Acetylenic Amides with Phenols. General Method of Synthesis of β -Substituted Derivatives of β -Phenoxyacrylamides. CHARLES MOUREU and I. LAZENNEC (*Compt. rend.*, 1906, 142, 894—895. Compare this vol., ii, 240, 276).—The β -substituted β -phenoxyacrylamides are obtained by heating at 130—140° the sodium derivative of phenol with the acetylenic amide dissolved in phenol. β -o-Tolylloxy- β -amylacrylamide,



and β -phenoxy- β -hexylacrylamide, $\text{C}_6\text{H}_{13}\cdot\text{C}(\text{OPh})\text{:CH}\cdot\text{CO}\cdot\text{NH}_2$, are oily substances. β -Phenoxy- β -phenylacrylamide, $\text{OPh}\cdot\text{CPh}\text{:CH}\cdot\text{CO}\cdot\text{NH}_2$, melts at 195—197°, β -o-tolylloxy- β -phenylacrylamide,



at 168°, and β -guaiacoxo- β -phenylacrylamide,



at 158°. When heated with dilute sulphuric acid, these substituted acrylamides are hydrolysed with the formation of the corresponding ketone and phenol; thus, β -phenoxy- β -hexylacrylamide yields methyl hexyl ketone and phenol. H. M. D.

Fermentation Vats. HERMANN WENDELSTADT and ARTHUR BINZ (*Ber.*, 1906, 39, 1627—1631).—Woad fermentations may be conducted on the small scale in glass vessels provided atmospheric oxygen is not allowed to enter. Experiments are most readily conducted in a litre flask provided with a cork and a delivery tube the end of which dips under water. Attempts have been made to isolate the characteristic organism which causes the fermentation. The addition of disinfectants, or sterilisation by heating, renders woad non-fermentable. J. J. S.

Linking Up of Amino-acids. HANS MEYER (*Ber.*, 1906, 39, 1451—1452).—A considerable amount of anthranilo-anthranilic acid (Anschütz, Schmidt, and Greiffenberg, *Abstr.*, 1903, i, 57; Mohr and Köhler, D.R.-P. 127138) is obtained as a by-product in the preparation of anthranilic acid according to D.R.-P. 55988. J. J. S.

Tautomerism of cycloHexanone. CARL MANNICH (*Ber.*, 1906, 39, 1594—1595).—When boiled with acetic anhydride and sodium acetate in a reflux apparatus, cyclohexanone forms *tetrahydrophenyl acetate*, $\text{C}_6\text{H}_9\cdot\text{O}\cdot\text{Ac}$, which is obtained as a colourless oil with a pleasant fruity odour. The acetate boils at 180—182°, is hydrolysed completely by boiling alcoholic potassium hydroxide, and when treated with semicarbazide hydrochloride and potassium hydroxide in dilute alcoholic solution yields the semicarbazone of cyclohexanone. In slightly alkaline solution, the acetate is oxidised by potassium permanganate, forming adipic acid. G. Y.

Ketones obtained by means of *n*-Valeric Acid. E. LAYRAUD (*Bull. Soc. chim.*, 1906, [iii], 35, 223—235).—Phenyl butyl ketone,

obtained by condensing valeryl chloride with benzene in presence of aluminium chloride, boils at 248.5° (corr.) and has $n_D 1.5152$ at 19° (compare Perkin and Calman, Trans., 1886, 49, 161). The *oxime* separates from ether in colourless, silky needles, melts at $52-52.5^{\circ}$, is readily soluble in alcohol or benzene, less so in light petroleum, and is converted by phosphorus pentachloride into a mixture of benzoyl-butylamine and valerylaniline. The *semicarbazone* crystallises from boiling alcohol in silky needles and melts at 166° .

p-Tolyl butyl ketone, similarly prepared, crystallises in bulky monoclinic prisms. The *oxime* is a viscous, colourless liquid and boils at 180° under 25 mm. or at 168° under 13 mm. pressure, and undergoes the Beckmann transformation with phosphorus pentachloride. The *semicarbazone* melts at 206° (compare Blaise, Abstr., 1902, i, 164).

p-Xylol butyl ketone ($\text{Me}_2 : \text{CO} = 1 : 4 : 6$), similarly prepared from *p*-xylene and valeryl chloride, is a colourless liquid of pleasant odour, boils at 266.5° under 762 mm. pressure, and is miscible with organic solvents. The *oxime* is oily and distils at $175-176^{\circ}$ under 19 mm. pressure. The *semicarbazone* is crystalline, melts at 139° , and is less soluble in alcohol than its lower homologue.

m-Xylol butyl ketone ($\text{Me}_2 : \text{CO} = 1 : 3 : 6$) is a slightly oily, colourless liquid and boils at 149° under 16 mm. pressure. On oxidation with chromic acid, dissolved in acetic acid, it yields 2:4-dimethylbenzoic acid. The *oxime* is a viscous, yellow liquid and distils at $184-187^{\circ}$ under 21 mm. pressure. The *semicarbazone* crystallises from boiling alcohol and melts at 188° .

p-Phenylethyl butyl ketone is a colourless liquid and boils at $163-164^{\circ}$ under 27 mm. pressure, or at $173-174^{\circ}$ under 33 mm. pressure. On oxidation with chromic acid dissolved in acetic acid, it yields *p*-ethylbenzoic acid. The *oxime* is a viscous liquid and boils at $193-194^{\circ}$ under 21 mm. pressure. The *semicarbazone* crystallises from boiling methyl alcohol and melts at 190.5° .

p-Anisyl butyl ketone crystallises in large prisms, melts at $27-28^{\circ}$, boils at 196.5° under 40 mm. pressure, and is readily soluble in alcohol and ether. On oxidation with chromic acid, it yields butyric and anisic acids. The *semicarbazone* crystallises from boiling alcohol, melts at 164° , and is slightly soluble in benzene or ether.

p-Phenetyl butyl ketone crystallises in colourless needles, melts at 31° , is almost inodorous, and on oxidation with chromic acid yields *p*-ethoxybenzoic acid. The *semicarbazone* crystallises in needles, melts at 192° , and is slightly soluble in light petroleum or benzene, more so in ether or chloroform.

T. A. H.

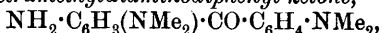
Behaviour of Ammonium Cyanide with Ketones of the Series $\text{CO}(\text{C}_n\text{H}_{2n-1})_2$. W. WIEKMANN (*Ber.*, 1906, 39, 1200. Compare this vol., i, 409, 426).—Ammonium cyanide does not interact with benzophenone or phenyl *p*-tolyl ketone in alcoholic solution at 80° under pressure.

G. Y.

Nitro-derivatives of Tetramethyldiaminobenzophenone. ALFRED KLIÉGL (*Ber.*, 1906, 39, 1266—1275. Compare Nathanson and Müller, Abstr., 1889, 1188; Grimaux, Abstr., 1898, i, 581).—The nitration of Michler's ketone is most readily effected by adding a

mixture of 66 per cent. nitric acid and concentrated sulphuric acid to a well-cooled solution of the ketone in concentrated sulphuric acid.

When the mono-nitro-derivative is reduced with stannous chloride and hydrochloric acid between -5° and $+5^{\circ}$, it gives a 50 per cent. yield of 3-amino-4 : 4'-tetramethyldiaminodiphenyl ketone,



which crystallises in dark yellow prisms melting at $138.75-139^{\circ}$ and dissolves only sparingly in ether. The *oxime*, $\text{C}_{17}\text{H}_{22}\text{ON}_4$, crystallises in intensely yellow needles, sinters at 192° , and melts at $194.5-196.5^{\circ}$. It dissolves sparingly in ether, benzene, or carbon tetrachloride. The *acetyl* derivative, $\text{C}_{19}\text{H}_{25}\text{O}_2\text{N}_3$, melts at $153.5-154.5^{\circ}$, crystallises from 70 per cent. alcohol and is only sparingly soluble in ether or light petroleum. The *benzoyl* derivative, $\text{C}_{24}\text{H}_{27}\text{O}_2\text{N}_3$, melts at $190.5-192.5^{\circ}$.

3-Acetylamino-4 : 4'-tetramethyldiaminobenzhydrol, $\text{C}_{19}\text{H}_{25}\text{O}_2\text{N}_3$, is obtained when the acetyl derivative of the ketone is reduced in the cold with zinc dust and 10-20 per cent. hydrochloric acid, and the filtered solution poured into sodium hydroxide solution at 0° . It crystallises from a mixture of acetone and water in thick, colourless prisms melting at $145.5-146^{\circ}$, is only sparingly soluble in ether or light petroleum, and gives a blue coloration when warmed with glacial acetic acid. The corresponding *benzoyl* derivative, $\text{C}_{24}\text{H}_{27}\text{O}_2\text{N}_3$, melts at $180.5-181.5^{\circ}$.

3 : 3'-Diamino-4 : 4'-tetramethyldiaminodiphenyl ketone, obtained by the reduction of the corresponding dinitro-compound with stannous chloride and hydrochloric acid in alcoholic solution at low temperatures, crystallises from alcohol or ethyl acetate in glistening, golden-yellow plates and melts at $145-145.5^{\circ}$. The *oxime* crystallises from benzene in slender, colourless needles having the composition $\text{C}_{17}\text{H}_{23}\text{ON}_5$, C_6H_6 . After loss of the benzene, it melts at 168° , and is readily decomposed by hydrochloric acid. The *benzoyl* derivative, $\text{C}_{31}\text{H}_{30}\text{O}_3\text{N}_4$, crystallises from glacial acetic acid in pale yellow plates melting at about $199.5-201^{\circ}$.

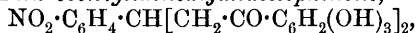
2-Acetylamino-4 : 4'-tetramethyldiaminodiphenylmethane (D.R.-P. 79250), obtained by acetylating Ullmann and Maric's 2-amino-4 : 4'-tetramethyldiaminodiphenylmethane (Abstr., 1902, i, 182), melts at 138° , and when oxidised with an alcoholic solution of chloranil yields 2-acetylamino-4 : 4'-tetramethyldiaminodiphenyl ketone, $\text{C}_{19}\text{H}_{23}\text{O}_2\text{N}_3$, which crystallises in lemon-yellow prisms melting at 162.25° and sparingly soluble in ether. When hydrolysed, it yields 2-amino-4 : 4'-tetramethyldiaminobenzophenone, melting at 205.5° , and quite distinct from the amino-compound obtained by reducing the mono-nitro-derivative of Michler's ketone, and hence the nitro-group in this latter occupies the position 3. 2-Acetylamino-4 : 4'-tetramethyldiaminobenzhydrol melts between 165° and 169° . J. J. S.

Action of Imino-esters and of Imino-chlorides on Organo-magnesium Derivatives. RAYMOND MARQUIS (*Compt. rend.*, 1906, 142, 711-713).—In addition to the methods already described by Blaise (Abstr., 1901, i, 133; 1902, i, 164) and by Béis (Abstr., 1904, i, 15) for the synthesis of ketones by means of organo-magnesium derivatives, the author finds that when methyl phenyliminobenzoate is heated at

100° with magnesium phenyl bromide in toluene solution, and the product decomposed by acid, benzophenoneanil is obtained, according to the equation $\text{OMe} \cdot \text{CPh} : \text{NPh} + \text{MgBrPh} = \text{MgBr} \cdot \text{OMe} + \text{CPh}_2 : \text{NPh}$, and this is readily converted into benzophenone on boiling with dilute acids, the yield being 55 per cent. of the theoretical. Attempts to extend the method to the preparation of mixed ketones were unsuccessful generally. Ethyl phenyliminobenzoate and magnesium benzyl chloride, however, interact to form deoxybenzoin (phenyl benzyl ketone) with a yield of 10 per cent. of the theoretical, whilst the yield is increased to 60 per cent. if benzoylphenyliminochloride replaces the ethyl phenyliminobenzoate in the above reaction. M. A. W.

Condensation Products of Gallacetophenone. HANS RUPE and L. VEIT (*Zeit. Farb. Ind.*, 1906, 5, 101—105).—*o*-Nitrobenzylidenegallacetophenone, $\text{C}_6\text{H}_2(\text{OH})_3 \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, prepared by condensing gallacetophenone with *o*-nitrobenzaldehyde by means of hydrogen chloride in alcoholic solution, crystallises from alcohol in long, lustrous, yellowish-green needles and melts at 212°. The triacetyl derivative, $\text{C}_{21}\text{H}_{17}\text{O}_9\text{N}$, crystallises from alcohol in small, yellow needles and decomposes at 165°.

On condensing triacetyl-gallacetophenone with *m*-nitrobenzaldehyde in presence of hydrogen chloride, *m*-nitrobenzylidenegallacetophenone, $\text{C}_{15}\text{H}_{11}\text{O}_6\text{N}$, or *m*-nitrobenzylidenedigallacetophenone,

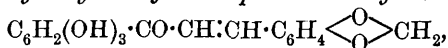


is obtained, the product depending on the conditions; the acetyl groups are eliminated during the condensation. *m*-Nitrobenzylidenegallacetophenone crystallises from alcohol in small needles, melts at 94°, and gives a triacetyl derivative, $\text{C}_{21}\text{H}_{17}\text{O}_9\text{N}$, which crystallises from glacial acetic acid in silver-white needles and melts at 152°. *m*-Nitrobenzylidenedigallacetophenone crystallises from alcohol on adding water in yellow needles, melts and decomposes at 220—230°, and gives a hexa-acetyl derivative, $\text{C}_{35}\text{H}_{31}\text{O}_{16}\text{N}$, which forms silver-white needles and melts at 193°.

p-Nitrobenzaldehyde also gives two derivatives with gallacetophenone. *p*-Nitrobenzylidenegallacetophenone crystallises from alcohol on adding water in golden-yellow needles, melts at 138°, and gives a triacetyl derivative which crystallises from alcohol in slender, silky needles and melts at 158°. *p*-Nitrobenzylidenedigallacetophenone crystallises from dilute alcohol in feebly yellow needles and melts and decomposes at 212°; the hexa-acetyl derivative, $\text{C}_{35}\text{H}_{31}\text{O}_{16}\text{N}$, crystallises from alcohol in white needles and melts and decomposes at 185°.

Attempts to condense protocatechualdehyde with triacetyl-gallacetophenone in presence of hydrogen chloride gave only resinous products; experiments made with the dibenzoyl derivative of protocatechualdehyde were equally unsuccessful.

3 : 4-Dihydroxybenzylidenegallacetophenone methylene ether,



prepared by condensing triacetyl-gallacetophenone with piperonal by means of hydrogen chloride, crystallises from benzene in long, golden-

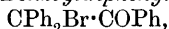
yellow needles, melts at 208° , and gives a *triacetyl* derivative, $C_{22}H_{18}O_6$, which crystallises from alcohol in yellow needles and melts at 142° .

The comparative tinctorial value of the substances enumerated above is dealt with. W. A. D.

The Varying Values of Single Bonds. ALFRED WERNER (*Ber.*, 1906, 39, 1278—1292).—It is well known that different groups of unsaturated compounds appear to be unsaturated to different degrees. The three groups of diphenylethylene, ordinary ethylene, and fulgene compounds are compared. The members of the first group cannot combine with bromine, those of the second combine readily, and those of the third can even abstract oxygen from the atmosphere.

It is suggested that when the atom M in the compound $M \cdot X$ is linked with other atoms, its affinity may be so lessened that the greater part of the saturation capacity of X is not utilised, and thus is available for the formation of molecular compounds with other substances. As examples are cited the numerous cases of the formation of additive compounds between metallic haloids and compounds such as $SnCl_4$, PCl_5 , PBr_5 , $WOCl$, $POCl_3$, $SeOCl_2$, NO_2Cl , &c. Organic compounds of the type CPh_3Cl , $AlCl_3$, CPh_3Cl , $SnCl_4$, $2(CPh_3Cl, 3HgCl_2)$, CPh_3Cl , $ZnCl_2$, and similar derivatives are also quoted. Experiments have proved that when the phenyl groups in the triphenylchloromethane are replaced by other negative groups, such as benzoyl, the products are not always so reactive as the triphenylmethane derivatives. Benzoyldiphenylbromomethane reacts with alcohols in the same manner as triphenylchloromethane, as does also benzoyldiphenylene bromomethane, but tribenzoylmethane may be boiled for hours with alcohols without decomposition. The reactivity of the haloid derivatives of triphenylmethane and their formation of additive compounds is attributed to the small saturation value of the CPh_3 group, and it is argued that in $CHPh_3$ there should be a considerable residual affinity of the H atom, and the compound should therefore yield additive derivatives. Several of these are cited.

[With PH. GERHARDT].—*Benzoyldiphenylbromomethane*,



obtained by brominating triphenylvinyl alcohol in chloroform solution, crystallises from a mixture of ether and light petroleum in colourless needles melting at 99° , and dissolves readily in most organic solvents. When boiled with methyl alcohol, it yields the *methyl ether* of benzoyldiphenylcarbinol, $OMe \cdot CPh_2 \cdot CPh$, which crystallises in colourless plates melting at 94° . The corresponding *ethyl ether* melts at 85° . When boiled with aqueous acetone, the bromo-derivative yields phenylbenzoin.

[With G. SCHÖLER].—*Benzoylfluorene*, $C_{20}H_{14}O$, obtained by the Claisen reaction from ethyl benzoate and fluorene, crystallises from methyl alcohol in long needles melting at 138° . *Benzoyldiphenylene-bromomethane*, $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > CBr \cdot CPh$, obtained by the action of bromine

on a benzene solution of benzoylfluorene, forms small, monoclinic

crystals melting at 145° . The *methyl ether*, $\text{C}_6\text{H}_4 > \text{C}(\text{OMe}) \cdot \text{COPh}$, separates from its solution in light petroleum as small, rhombic crystals.

[With W. ZIPSER.]—*Tribenzoylbromomethane*, $\text{CBr}(\text{COPh})_3$, obtained by brominating a chloroform solution of tribenzoylmethane, crystallises from ether in glistening needles and melts at 89° .

[With A. SUMMERER.]—Triphenylmethane forms an *additive* product with aniline, $\text{CHPh}_3 \cdot \text{NH}_2\text{Ph}$, in the form of colourless, cubical crystals melting at 84° . The *o*-toluidine additive *compound* forms large, transparent, rhombic plates.

m-Nitrophenylnaphthaxanthen (Zenoni, Abstr., 1894, i, 136) forms an additive compound, $\text{C}_{33}\text{H}_{23}\text{O}_3\text{N}$, with benzene in the form of yellow, glistening crystals.

Ethyl tetranitrodiphenylacetate (Richter, Ber., 1888, 21, 2471) is best prepared by nitrating ethyl diphenylacetate. It yields an *additive* compound, $\text{C}_{22}\text{H}_{19}\text{O}_{10}\text{N}_5$, with aniline, which separates from alcohol as a voluminous, golden-yellow precipitate. When exposed to the air or heated at 91° , it turns black and melts and decomposes at 96.5° . The *additive* compound with naphthalene, $\text{C}_{42}\text{H}_{32}\text{O}_{20}\text{N}_8$, crystallises in colourless needles melting at 156° . J. J. S.

Synthesis of a Ketone of the *cyclo*Butane Series. EDGAR WEDEKIND and W. WEISSWANGE (Ber., 1906, 39, 1631—1646).—

1 : 3-*Diketotetramethylcyclobutane*, $\text{CMe}_2 < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{CMe}_2$, is obtained when a solution of *isobutyryl* chloride in dry carbon disulphide is dropped into a solution of triethylamine in the same solvent, great care being taken that all the substances are dry and that atmospheric moisture is excluded. After removal of trimethylamine hydrochloride, an oil is obtained from which crystals of the ketone gradually separate; they are most readily purified by washing with light petroleum and then subliming. The yield is under 20 per cent. The ketone has an odour resembling that of menthol or camphor, is extremely volatile, and passes over with ether vapour. It crystallises well, melts at 115 — 116° , has n_D 1.4991 at 15° and a sp. gr. 0.8875, dissolves readily in most organic solvents with the exception of light petroleum, but is only sparingly soluble in water. It gives no coloration with ferric chloride and does not decolorise bromine or permanganate. With ammonia at 120 — 130° , it yields a product melting at 108° . The *dioxime*, $\text{C}_8\text{H}_4\text{O}_2\text{N}_2$, crystallises from alcohol in colourless plates melting at 281° and is insoluble in water or ether. The *bisphenylhydrazone*, $\text{C}_{20}\text{H}_{24}\text{N}_4$, forms colourless plates melting at 207 — 208° , and does not give Fechner's osazone reaction. The *disemicarbazone*, $\text{C}_{10}\text{H}_{18}\text{O}_2\text{N}_6$, begins to sinter at 282° and melts and decomposes at 298° . The ketone condenses with *o*-phenylenediamine yielding a *product*, $\text{C}_{14}\text{H}_{18}\text{ON}_2$, which crystallises from boiling ethyl acetate in glistening plates melting at 248 — 249° . It yields an *acetyl* derivative melting at 150 — 151° and does not give the ordinary quinoxaline reactions.

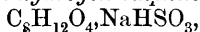
[With L. ERDMANN.]—Tetramethyldiketocyclobutane can also be

obtained by the action of the copper-zinc couple on a dry ethereal solution of α -bromoisobutyryl bromide. The condensation product with phenylcarbimide, $C_{11}H_{11}O_2N$, melts at 239° . J. J. S.

1-Methylcyclopentane-2:4:5-trione. I. OTTO DIELS, JOHANNES SIELISCH, and ERNST MÜLLER (*Ber.*, 1906, 39, 1328—1340).—Since acetone condenses with ethyl oxalate to form oxalyldiacetone, ethyl acetoneoxalate, or ethyl acetonedioxalate, according to the experimental conditions, and since substituted acetones, such as dibenzyl ketone, differ from acetone itself in forming cyclic triketones with ethyl oxalate, the authors have studied the condensation of methyl ethyl ketone with ethyl oxalate.

γ - δ -Decanetetrone, $CH_3Me \cdot CO \cdot CH_2 \cdot CO \cdot CO \cdot CH_2 \cdot CO \cdot CH_2Me$, prepared by the condensation of methyl ethyl ketone with ethyl oxalate in the presence of sodium, is a yellowish-white solid and melts at 75 — 76° . Its solutions are intensely yellow. Its *dioxime* separates from alcohol in colourless leaflets and melts at 180° .

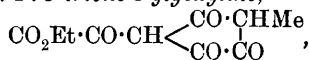
Ethyl propionylpyruvate, $CH_3Me \cdot CO \cdot CH_2 \cdot CO \cdot CO_2Et$, prepared by the condensation of methyl ethyl ketone with ethyl oxalate in the presence of sodium ethoxide, boils at 73 — 78° under 0.6 mm. pressure; it is a faintly yellow oil with a characteristic odour. It forms sparingly soluble metallic salts, and gives a dark red coloration with ferric chloride. Its *sodium hydrogen sulphite additive compound*,



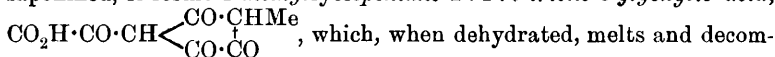
crystallises in colourless leaflets.

When heated at 120° with concentrated hydrochloric acid, ethyl propionylpyruvate forms *propionylpyruvic acid*, which separates from water in colourless crystals containing H_2O and melts at 63 — 65° ; the anhydrous acid melts at 83.5° . The aqueous solution gives a dark red coloration with ferric chloride.

By variation of the conditions of the condensation of methyl ethyl ketone and ethyl oxalate in the presence of sodium ethoxide, *ethyl 1-methylcyclopentane-2:4:5-trione-3-glyoxylate*,



is formed, melting at 161° ; its solutions are strongly yellow. When saponified, it forms *1-methylcyclopentane-2:4:5-trione-3-glyoxylic acid*,



which, when dehydrated, melts and decomposes at 193° ; it separates from ethyl acetate in prismatic needles which are green and darker in colour than the ester. Its *dimethyl-aniline* salt melts at 151.5° .

1-Methylcyclopentane-2:4:5-trione, $CH_2 \begin{array}{c} \diagup CO \cdot CHMe \\ \diagdown CO \cdot CO \end{array}$, prepared by

boiling the ethyl methylcyclopentanetrione-glyoxylate described with dilute hydrochloric acid, separates from water in colourless needles containing $1H_2O$, melts at 78.5 — 79.5° , or at 118° when dehydrated; its aqueous solution gives a red coloration with ferric chloride. Its *oxime* melts at 216 — 217° .

The proximity of two carbonyl groups in the molecule of the ketone

is indicated by the formation with *o*-phenylenediamine of a normally constituted *quinoxaline* derivative, which melts indefinitely at about 317°.

The action of bromine on the ketone yields *dibromomethylcyclopentanetrione*, $\text{CHBr} \begin{smallmatrix} \diagup \text{CO} \cdot \text{CBrMe} \\ \diagdown \text{CO} \cdot \text{CO} \end{smallmatrix}$, which crystallises in slightly coloured leaflets and melts at 182°. Like the parent ketone, it acts as a monobasic acid.

The *methyl ether* of the *methylcyclopentanetrione* melts at 51°.

The presence of an acid methylene group in the molecule of the ketone is shown by the action of benzaldehyde on the ketone, when the *benzylidene* derivative, $\text{CHPh} \cdot \text{C} \begin{smallmatrix} \diagup \text{CO} \cdot \text{CHMe} \\ \diagdown \text{CO} \cdot \text{CO} \end{smallmatrix}$, is formed; it separates from methyl alcohol in yellow prisms and melts at 194—195°; its solution in alkalis is yellow; the *benzylidene* derivative forms an *aniline* salt which melts at 132°. A. McK.

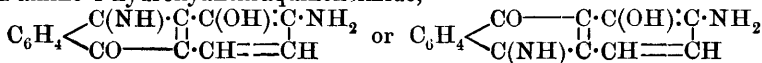
1:4-Anthraquinone. KASIMIR LAGODZINSKI (*Ber.*, 1906, 39, 1717—1718)—1-Anthrol combines with diazonium salts to form azo-compounds which are reduced in acid or alkaline solution to 1:4-aminoanthrol, the hydrochloride of which is oxidised by ferric chloride to 1:4-anthraquinone (Dienel, this vol., i, 290). C. S.

The Influence of Catalysts on Substitution in the Aromatic Nucleus. KARL HOLDERMANN (*Ber.*, 1906, 39, 1250—1258).—Attention is drawn to the influence which mercury salts and boric acid have on the sulphonation of anthraquinone (Düschmann; Liebermann & Pleus, *Abstr.*, 1904, i, 326; *Farbenfabriken vorm. F. Bayer & Co.*, this vol., i, 293). Relatively large amounts of boric acid are required, and its influence is attributed to the formation of esters. Minute quantities of mercury salts, on the other hand, are sufficient.

The addition of small amounts of mercury on mercurous sulphate has no effect on the sulphonation of toluene, benzoic acid, or α -naphthol. The addition of mercury to a mixture of aniline and sulphuric acid produces oxidation rather than sulphonation, and if the temperature is kept at 125—130° small amounts of benzidine and a red oil are obtained. Reduced nickel and copper have no catalytic action on these preparations.

Mercury, copper, cobalt, and nickel have no effect on the nitration of toluene or nitrobenzene, but mercuric nitrate appears to have a considerable influence on the nitration of anthraquinone and its β -methyl derivative. J. J. S.

Action of Ammonia on Alizarin. ROLAND SCHOLL and M. PARTHEY (*Ber.*, 1906, 39, 1201—1206. Compare Prud'homme, this vol., i, 193; Noetling and Wortmann, *ibid.*, 291).—Perger's 1:2-diaminoanthraquinone (*Abstr.*, 1879, 254, 724), formed by the action of concentrated aqueous ammonia on alizarin at 140° under pressure, is 2-amino-1-hydroxyanthraquinoneimide,

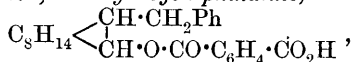


It commences to decompose and evolve ammonia at 250° , melts at about 280° , dissolves in dilute alkali hydroxides or acids, forming solutions from which it is reprecipitated on neutralisation, and when boiled with glacial acetic acid yields 2-acetyl-amino-1-hydroxyanthraquinone melting at 242° . The *potassium* derivative, $C_{14}H_9O_2N_2K, CH_4O$, was analysed. The *acetyl* derivative, $C_6H_4 \begin{smallmatrix} C(NH) \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} C_6H_2(OH) \cdot NHAc$, is obtained as a red, crystalline powder, which commences to decompose at 225° .

Liebermann's alizarinimide and ammonium derivative of alizarinimide (this Journal, 1877, i, 613) are identical with 2-amino-1-hydroxyanthraquinone and 2-amino-1-hydroxyanthraquinoneimide respectively. G. Y.

Preparation of Borneol and Bornyl Acetate from Pinene Hydrochloride. JOSEF HOUBEN (*Ber.*, 1906, 39, 1700—1702. Compare Abstr., this vol., i, 21).—A current of dry air or oxygen is passed through the ethereal solution containing the product of the reaction between pinene hydrochloride, magnesium, and a trace of methyl iodide; subsequent treatment with ice and sulphuric acid or with ice and acetic anhydride yields borneol or bornyl acetate respectively. C. S.

Benzyl- and Phenyl-borneols and their Products of Dehydration, Benzyl- and Phenyl-camphenes. ALBIN HALLER and E. BAUER (*Compt. rend.*, 1906, 142, 677—681).—*α-Benzylborneol*, $C_8H_{14} \begin{smallmatrix} CH \cdot CH_2Ph \\ | \\ CH \cdot OH \end{smallmatrix}$, prepared by reducing benzylcamphor or benzylidenecamphor by means of sodium and alcohol, is a viscous oil which boils at 179 — 181° under 13 mm. pressure, has a sp. gr. 1.1325 at $18^{\circ}/4^{\circ}$, and $[\alpha]_D + 26^{\circ}10'$; the *phenylurethane* crystallises in white crusts from a mixture of ether and light petroleum, melts at 116 — 118° , and has $[\alpha]_D - 21^{\circ}17'$; the *hydrogen phthalate*,



is crystalline, melts at 146° , and has $[\alpha]_D + 46^{\circ}8'$.

α-Benzylcamphene, $C_8H_{14} \begin{smallmatrix} C \cdot CH_2Ph \\ | \\ CH \end{smallmatrix}$, is formed when *α*-benzyl-

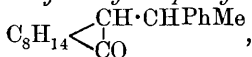
borneol is dehydrated by means of phthalic anhydride, anhydrous formic acid, or pyruvic acid (compare Bouveault and Blanc, Abstr., 1905, i, 222); it boils at 170 — 171° under 20 mm. pressure or 160 — 161° under 10 mm. pressure, but the specific rotation varies in the different preparations, being $8^{\circ}20'$, $5^{\circ}20'$, or $1^{\circ}25'$, according as phthalic anhydride, formic acid, or pyruvic acid is the dehydrating agent employed.

β-Benzylborneol, $C_8H_{14} \begin{smallmatrix} CH_2 \\ | \\ C(OH) \cdot CH_2Ph \end{smallmatrix}$, formed by the action of magnesium phenyl bromide on camphor, is an oil which boils at 169 — 170° under 10 to 11 mm. pressure, has $[\alpha]_D - 12^{\circ}0'$, forms a crystalline derivative with formic acid, and yields *β*-benzylcamphene,

$C_8H_{14} \begin{smallmatrix} CH \\ | \\ C-CH_2Ph \end{smallmatrix}$, when dehydrated by means of pyruvic acid, anhydrous formic acid, or phthalic anhydride. This hydrocarbon forms white needles, melts at 24° , boils at $150-161^\circ$ under 11 mm. pressure, has $[\alpha]_D - 60^\circ 44'$, forms a white crystalline additive compound with hydrogen bromide, which melts at $63-64^\circ$, and is oxidised by potassium permanganate, forming a mixture of benzoic and camphoric acids.

β -Phenylborneol, $C_8H_{14} \begin{smallmatrix} CH_2 \\ | \\ CPh \cdot OH \end{smallmatrix}$, prepared in a similar manner to the corresponding benzyl compound, is a crystalline compound which melts at $40-41^\circ$ and boils at $157-158^\circ$ under 12 mm. pressure; when dehydrated by means of pyruvic acid, it yields β -phenylcamphene, $C_8H_{14} \begin{smallmatrix} CH \\ | \\ CPh \end{smallmatrix}$, which is an oil boiling at $138-141^\circ$ under 10 mm. pressure, and having a sp. gr. 0.9736 at $18^\circ/11^\circ$ and $[\alpha]_D + 7^\circ 15'$.
M. A. W.

**Diphenyl- or Alkylphenyl-camphoryl-methanes and-methyl-
enes**, $C_8H_{14} \begin{smallmatrix} CH \cdot CHRR' \\ | \\ CO \end{smallmatrix}$ and $C_8H_{14} \begin{smallmatrix} C \cdot CRR' \\ | \\ CO \end{smallmatrix}$. ALBIN HALLER and E. BAUER (*Compt. rend.*, 1906, 142, 971-976).—Benzylidenecamphor reacts with organo-magnesium derivatives to form the corresponding substituted phenylcamphorylmethanes, and the following compounds were thus prepared. *Phenylmethylcamphorylmethane*,



forms white crystals melting at $70-71^\circ$, and soluble in alcohol or benzene. *Phenylethylcamphorylmethane*, $C_8H_{14} \begin{smallmatrix} CH \cdot CHPhEt \\ | \\ CO \end{smallmatrix}$,

forms white crystals melting at 80° . *Phenylbenzylcamphorylmethane*, $C_8H_{14} \begin{smallmatrix} CH \cdot CHPh \cdot CH_2Ph \\ | \\ CO \end{smallmatrix}$, forms a thick oil boiling at 230° under 10 mm. pressure and has $[\alpha]_D + 90^\circ 49'$ in absolute alcohol.

Diphenylcamphorylmethane, $C_8H_{14} \begin{smallmatrix} CH \cdot CHPh_2 \\ | \\ CO \end{smallmatrix}$, forms well-defined white crystals melting at $106-107^\circ$ and has $[\alpha]_D + 62^\circ$; the same compound is also obtained by reducing diphenylcamphorylmethylene (see below) with sodium amalgam, but the specific rotation of the compound thus prepared varies from $+80^\circ 10'$ to $40^\circ 29'$.

Diphenylcamphorylmethylene, $C_8H_{14} \begin{smallmatrix} C \cdot CPh_2 \\ | \\ CO \end{smallmatrix}$, obtained by the action of benzophenone on the sodium derivative of camphor, boils at 250° under 15 mm. pressure, and crystallises from a mixture of ether and light petroleum in the form of magnificent yellow octahedra, which melt at 113.5° ; it has $[\alpha]_D + 287^\circ$ in alcoholic solution; the same compound is also obtained as a by-product in the preparation of diphenylcamphorylcarbinol, which has $[\alpha]_D + 62^\circ 49'$ (Malmgren, *Abstr.*, 1903, i, 103, 711), or by the dehydration of the carbinol by means of

anhydrous formic acid or pyruvic acid; the chief product of the latter reaction is, however, a compound, $C_{23}H_{26}O_2$, which forms a white solid melting at 200° .
M. A. W.

The Pinene Fractions of French and American Turpentine Oils. BERTEL AHLSTRÖM and OSSIAN ASCHAN (*Ber.*, 1906, 39, 1441—1446).—Ten or eleven fractions, collected from French and American turpentine respectively between 153° and 175° , showed continual diminution in rotatory power, accompanied in the latter case by change of sign. From a comparison of the rotations of the hydrochlorides of these fractions, the author considers that the two oils contain a common constituent, which is possibly nopinene (Semmler's pseudopinene, *Abstr.*, 1900, i, 452). The yield of nopinic acid is about fifteen times as great from the higher-boiling as from the lower-boiling fractions of American turpentine.
C. S.

Terpenes from Finnish Pine and Fir Resins. OSSIAN ASCHAN (*Ber.*, 1906, 39, 1447—1451. Compare Aschan and Hjelt, *Abstr.*, 1895, i, 545).—The resin from Finland pine, *Pinus sylvestris*, gives 9.2 per cent. of terpenes boiling below 180° , from which pinene and sylvestrene have been isolated. The fraction 155 — 160° has a sp. gr. 0.8657 and $[\alpha]_D + 20.22^\circ$.

The resin from the fir, *Pinus abies*, contains only 4.5 per cent. of terpenes. The fraction 155 — 160° has $[\alpha]_D - 7.87^\circ$, and *l*-pinene and also *l*-limonene have been isolated, the latter in the form of dipentene dihydrochloride. Sylvestrene could not be detected.
J. J. S.

Patchouli and Citronella Oils from Perak, Federated Malay States (*Bull. Imp. Inst.*, 1905, 3, 228—230).—The patchouli oil was dark lemon-yellow, had a sp. gr. 0.9525, $n_D 1.5063$, $\alpha_D - 43^\circ 31'$ in a 100 mm. tube, and was soluble in 90 per cent. alcohol to the extent of one volume in 7.4 volumes.

The citronella oil was pale yellow, had a sp. gr. 0.8948 at 15° , $n_D 1.4858$ at 24° , $\alpha_D - 1^\circ 34'$ at 24° in a 100 mm. tube, and was soluble in an equal volume of 80 per cent. alcohol. It contained 32.7 per cent. of geraniol and 55.3 per cent. of citronellal.
E. G.

Guaiacum Resin. PAUL RICHTER (*Arch. Pharm.*, 1906, 244, 90—119).—When submitted to dry distillation under 22 mm. pressure, the resin yielded 60 per cent. of distillate, boiling at 80 — 270° , whilst porous, shining charcoal remained in the retort. By means of distillation with steam, solution in aqueous sodium hydroxide, and fractional distillation, there were isolated from the distillate: tiglic aldehyde, guaiacol, cresol, pyroguaiacol, and a substance which boiled at 255 — 260° under 4 mm. pressure, resinous in character at first, but yielding crystals by slow evaporation of its solution in benzene and light petroleum. This melts at 107° , has the composition $C_{19}H_{20}O_5$, dissolves in aqueous alkali hydroxides but not in alkali carbonates, forms a *dibenzoyl* derivative melting at 143° , and is not affected by fusion with potassium hydroxide.

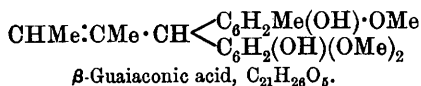
Guaiaconic acid was submitted to dry distillation very slowly under 22 mm. pressure. It yielded upwards of 60 per cent. of distillate at 80—280°, from which there were isolated : tiglic aldehyde, guaiacol, the substance described above melting at 107°, a crystalline *substance*, $C_{16}H_{18}O_3$, melting at 133°, and soluble in aqueous alkali hydroxides but not in alkali carbonates, and a resinous *substance*, $C_{34}H_{38}O_7$, which boils at 270—273° under 22 mm. pressure, dissolves in aqueous alkalis, but not in alkali carbonates, forms a powdery *tribenzoyl* derivative, which melts at 77—78° and is insoluble in aqueous alkalis, and gives a blue coloration with oxidising agents. In another experiment, where the guaiaconic acid was distilled under 22 mm. pressure as rapidly as possible, it yielded 65 per cent. of distillate, from which there were isolated : tiglic aldehyde, guaiacol, a small quantity of a crystalline *substance* melting at 203°, a syrupy *substance*, $C_{14}H_{16}O_4$, which boils at 170—174° under 22 mm. pressure, dissolves in aqueous alkali hydroxides, forms a crystalline *dibenzoyl* derivative melting at 103°, darkens in the air, and gives a green coloration with alcoholic ferric chloride, pyroguaiacol, and the substance described above as boiling at 270—273° under 22 mm. pressure.

Guaiaconic acid was isolated from guaiacum resin by extracting a mixture of the latter with sand with boiling benzene, concentrating the extract, and precipitating it with light petroleum. The precipitate was mixed with sand and extracted with ether, to which chloroform was added as the extraction progressed, the extract was then run in a thin stream into light petroleum. The guaiaconic acid thus precipitated was dissolved in benzene and the solution set aside. From the solution, β -guaiaconic acid, $C_{21}H_{26}O_5$, crystallised in small rhombohedra ; this melts at 127°, forms a *dibenzoyl* derivative which melts at 138°, is insoluble in aqueous alkali hydroxides, and is not converted by oxidising agents into any blue substance. The benzene mother liquor contained α -guaiaconic acid, $C_{22}H_{26}O_6$ or $C_{22}H_{24}O_6$, which was obtained as a light powder by pouring a solution of it in ether and chloroform into light petroleum ; it melts at 73° to a green liquid which turns brown at 101°, forms a *tribenzoyl* derivative which melts at 133—135°, is insoluble in aqueous alkalis, changes to a blue substance in the air or under the influence of oxidising agents, and when boiled with sulphurous acid retains the same composition, but melts at 101° to a brown liquid, without first turning green at 71°. Operations with this substance and with the crude guaiaconic acid were conducted in the dark.

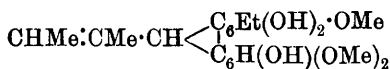
Guaiacum-blue, $C_{22}H_{24}O_9$, was obtained by shaking a 5 per cent. chloroform solution of α -guaiaconic acid with lead dioxide, added a little at a time, filtering the solution, and evaporating it under diminished pressure. It forms a dark blue powder ; it is reduced by sulphurous acid at 50° to α -guaiaconic acid melting at 99—101° to a brown liquid without first turning green at 72° ; when heated at 100°, it loses oxygen and leaves a brown residue, $C_{22}H_{24}O_7$, which melts at 85° and is converted into the blue substance by oxidising agents when heated at 120°, it leaves a residue of α -guaiaconic acid.

The following constitutional formulæ are suggested :

h h 2



β -Guaiaconic acid, $\text{C}_{21}\text{H}_{26}\text{O}_5$.



α -Guaiaconic acid, $\text{C}_{22}\text{H}_{26}\text{O}_6$.

C. F. B.

Effect of Heat on the Toxicity of Bitter Almonds. GIUSEPPE VELARDI (*Chem. Centr.*, 1906, i, 1030; from *Boll. Chim. Farm.*, 45, 65—67).—The following experiments on the effect of heat on the action of the emulsin on the amygdalin in bitter almonds were suggested by a case of poisoning. Whole and sliced almonds were heated in an air-bath at a constant temperature for two hours; they were then boiled with water and the distillate tested for hydrocyanic acid by means of the Prussian-blue reaction. It was found that at temperatures below 103° hydrocyanic acid was formed, but that at 105° the whole almonds alone showed the presence of a trace. At temperatures above 105° , hydrocyanic acid was not liberated, but the acid was formed when the almonds were macerated with powdered sweet almonds. Above 150° , hydrocyanic acid was only formed after several hours, and at 166° a day's heating was required. In all the experiments, the whole almonds withstood the action of heat better than the cut almonds and were found to contain a trace of hydrocyanic acid even after heating at 170° .

Pure amygdalin from Schuchardt melted at 208 — 210° when rapidly heated, but when slowly heated began to turn brown at 170° and melted at 180° , forming a resinous mass which contained 4.09 per cent. of nitrogen and was soluble in water, but only sparingly so in 65 per cent. alcohol; when treated with powdered sweet almonds and water, hydrocyanic acid was formed. The sample of amygdalin before heating contained 2.96 per cent. of nitrogen. Since a temperature of 170° is required to render the amygdalin incapable of being attacked by ferments, it is necessary to heat to this temperature to destroy the toxicity of bitter almonds. E. W. W.

Preparation of Blue and Violet Dyes by Oxidation. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 162625 and 162626).—Fast blue, violet, or in some cases black dyes are obtained by oxidising *p*-amino-, *p*-aminohydroxy-, or *p*-diamino-derivatives of diphenylamine, mixed with primary, secondary, or tertiary *m*-aminophenols, *m*-diamines, alkylated *m*-diamines, phenols, naphthols, hydroxycarboxylic acids, or *o*-aminophenol ethers. The components are mixed on the fibre with the oxidising agent, preferably a chlorate, and developed by heat. Acids are not added, salts such as aluminium chloride being preferable. Oxygen carriers, such as cerium salts, may or may not be added. C. H. D.

Certain Properties of Dye-bases and Dye-acids. LEONOR MICHAELIS (*Beitr. chem. Physiol. Path.*, 1906, 8, 38—50).—An aqueous

solution of Nile-blue base may be obtained by the addition of a little alkali hydroxide to a very dilute solution of the sulphate of the base. Examination with the ultramicroscope proves that the solution is in reality a suspension, and exposure to sunlight rapidly causes the formation of visible particles. Pseudo-solutions of practically all thiazines and oxazines are coagulated by light in a similar manner.

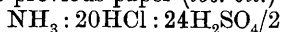
When sodium hydroxide solution is added to an aqueous solution of methylene-azure hydrochloride, a blue or bluish-violet solution is obtained, which can be preserved in the dark for some time, but turns red on exposure to light, and ultimately deposits a precipitate. The action of light is of a permanent nature, as the red solution when acidified yields a blue solution which, on the addition of alkali, turns red even in the dark. The red product is termed *photoazure*, and is also formed when methylene-blue solution is made alkaline and then exposed to sunlight.

True aqueous solutions of dye-bases, either in the form of the free bases (for example, methylene-blue base) or as salts (methylene-blue or Nile-blue), readily dye sections of organs (kidney, liver, spleen, or lymph-glands), especially the nuclei of the cells, whereas toluene solutions of the dye-bases or their salts do not stain the nuclei. The protoplasm colorations thus obtained are not stable in the presence of alcohol, and the colorations produced by aqueous and xylene solutions of the dye-salts are different: the former dissolve in Canada balsam, the latter do not.

Aqueous and xylene solutions of eosin-acid have much the same effect on sections of organs.

J. J. S.

Process of Dyeing Animal Textile Fibres. II. P. GELMO and WILHELM SUIDA (*Monatsh.*, 1906, 27, 225—235. Compare Abstr., 1905, i, 714).—The proportion in which two specimens of wool were found to absorb ammonia, hydrochloric acid, and sulphuric acid should have been given in the previous paper (*loc. cit.*) as



and $\text{NH}_3 : 20\text{HCl} : 21\text{H}_2\text{SO}_4/2$ respectively, instead of 1 : 2 : 2.4 and 1 : 2 : 2.1. Wool has therefore stronger basic properties than was then supposed.

Samples of a wool were boiled with distilled water, dilute hydrochloric acid, dilute ammonia, and aqueous sodium carbonate for one, twenty-one, and sixty hours, thoroughly washed with water, and titrated with *N*/10 sulphuric acid, *N*/10 hydrochloric acid, and *N*/10 ammonia. The aqueous extract had an odour of hydrogen sulphide and ammonia, and contained organic substances of the nature of peptone. Ammonia, hydrochloric acid, and sulphuric acid, were absorbed in the following proportions: by the untreated wool, $\text{NH}_3 : 17.3\text{HCl} : 20.3\text{H}_2\text{SO}_4/2$; by the wool after treatment for one hour with water, $\text{NH}_3 : 8.1\text{HCl} : 9.3\text{H}_2\text{SO}_4/2$; with hydrochloric acid, $\text{NH}_3 : 3.6\text{HCl} : 3.8\text{H}_2\text{SO}_4/2$; with ammonia, $\text{NH}_3 : 8.4\text{HCl} : 19.1\text{H}_2\text{SO}_4/2$; or with sodium carbonate, $\text{NH}_3 : 9.4\text{HCl} : 9.9\text{H}_2\text{SO}_4/2$.

On further treatment of the wool with water, hydrochloric acid, or ammonia, its acidity increases only slowly, whilst even on prolonged boiling with water or ammonia the basicity remains unchanged. The

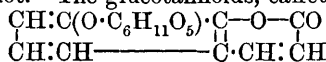
increase of the acidity over the somewhat diminished basicity is more marked on prolonged treatment of the wool with hydrochloric acid. When the wool is boiled with aqueous sodium carbonate, the relation of the acidity to the basicity rapidly becomes constant.

After being boiled with water, ammonia, or dilute sodium carbonate, the wool behaves towards crystal-violet, or crystal-ponceau, in the same manner as before treatment, but the shades obtained on dyeing the treated wool with crystal-violet are slightly less fast, whilst those obtained on dyeing the wool, after treatment with hydrochloric acid, with crystal-violet or crystal-ponceau show little fastness to soaping.

When boiled with alcoholic sulphuric acid, wool forms a sulphate, as, after being washed thoroughly with water, it still retains sulphuric acid, which is removed entirely when the wool is boiled with ammonium carbonate.

Wool which has been treated with water, hydrochloric acid, ammonia, or aqueous sodium carbonate gives more intense colorations with diazobenzenesulphonic acid (Pauly and Binz, *Abstr.*, 1905, i, 75) and with Millon's reagent than does the untreated wool. This points to an increase of phenolic hydroxyl groups during the treatment, and, with the other facts described, is explained by assuming the presence of lactone groups, $R \cdot CO \cdot O \cdot R'$, in wool. G. Y.

Constitution of Tannins. MAXIMILIAN NIERENSTEIN (*Chem. Centr.*, 1906, i, 940—941; from *Collegium*, 1906, 45—49. Compare *Abstr.*, 1905, i, 914).—The tannins are assumed to be derived from a hypothetical parent substance, tannone, $COPh \cdot OPh$, tannin itself being regarded as pentahydroxytannonecarboxylic acid. Some evidence as to the group which confers the "tannoid" character on the tannins is afforded by the fact that gallic acid gives a precipitate with sodium chloride and gelatin. Salicylic, protocatechuic, 2 : 4-dihydroxybenzoic and vanillic acids and the methyl ether of 2 : 4-dihydroxybenzoic acid, the methyl, dimethyl, and trimethyl ethers of gallic acid, and the 4-methyl ether of gallic acid (compare Graebe and Martz, *Abstr.*, 1903, i, 262) also give this reaction, whilst resorcinol, phloroglucinol, methyl gallate, methyl protocatechuate, and methyl 2 : 4-dihydroxybenzoate do not. The precipitation of gelatin is thus caused by the carboxyl group, but aromatic hydroxycarboxylic acids are not therefore to be regarded as tannins. That the CO group has a tannaphore character is also shown by the fact that whilst hexahydroxyaurincarboxylic acid precipitates gelatin, the hexahydroxydiphenylmethanedicarboxylic acid which is formed simultaneously (compare Kunz-Krause, *Abstr.*, 1897, i, 530) does not. The glucotannoids, caffetannic acid,



and fabiantannic acid, $C_6H_{11}O_5 \cdot O \cdot C:CH \cdot C-O-CO$, contain a tannaphore CO group. A CO group of this character is also present in fustintannic, morintannic, and ellagotannic acids, the constitution of which is uncertain. E. W. W.

Dimethylpyrone Methiodide. FRIEDRICH KEHRMANN and ALFRED DUTTENHÖFER (*Ber.*, 1906, **39**, 1299—1304).—When a mixture of molecular amounts of dimethylpyrone and methyl sulphate is left at the ordinary temperature for several weeks, and a saturated aqueous solution of potassium iodide is then added to a solution of the product in little water, *dimethylpyrone methiodide*, $C_8H_{11}O_2I$, separates. It forms yellowish-white, glistening needles, and is slightly acid towards litmus. When its solution in water or in ethyl alcohol is heated, or when the solid is heated quickly above 100° , methyl iodide is evolved.

Dimethylpyrone methochloride platinichloride, $(C_8H_{11}O_2Cl)_2PtCl_4$, prepared by the addition of an excess of sodium platinichloride to the concentrated aqueous solution of dimethylpyrone methosulphate, evolves methyl chloride when quickly heated at 158° . When its aqueous solution is boiled for several minutes and then cooled, a portion of the original substance separates in orange-coloured leaflets, whilst the remainder is converted into dimethylpyrone platinichloride.

A. McK.

α -Naphthaflavonol. GERTRUD WOKER (*Ber.*, 1906, **39**, 1649—1653).— *α -Naphthaflavanone*, $C_{10}H_6 \begin{smallmatrix} \diagup O-CHPh \\ \diagdown CO \cdot CH_2 \end{smallmatrix}$, prepared by heating the corresponding chalcone in alcoholic solution with hydrochloric acid (compare Kostanecki, Lampe, and Tambor, *Abstr.*, 1904, i, 441), separates from alcohol in prisms and melts at 126° . The solution in alcohol is colourless, but exhibits a bluish-violet fluorescence.

Its *isonitroso*-derivative, $C_{10}H_6 \begin{smallmatrix} \diagup O-CHPh \\ \diagdown CO \cdot C \cdot N \cdot OH \end{smallmatrix}$, prepared by the action of amyl nitrite on the preceding compound, crystallises from alcohol in glistening, yellow leaflets and melts at 173 — 174° . Its solution in alcohol is yellowish-red and exhibits a green fluorescence.

α -Naphthaflavonol, $C_{10}H_6 \begin{smallmatrix} \diagup O-CHPh \\ \diagdown CO \cdot C \cdot OH \end{smallmatrix}$, prepared by hydrolysing the preceding compound with dilute sulphuric acid, separates from alcohol in green, iridescent leaflets and melts at 210° . It exhibits a marked fluorescence. Its *acetyl* derivative crystallises from alcohol in glistening leaflets and melts at 194 — 195° .

α -Naphthaflavone, $C_{10}H_6 \begin{smallmatrix} \diagup O-CPh \\ \diagdown CO \cdot CH \end{smallmatrix}$, prepared by replacing a hydrogen atom in the α -position in *α -naphthaflavanone* by bromine and then acting on the resulting bromo-compound with alkali, melts at 154 — 156° and is identical with the compound prepared by Kostanecki by the aid of 2-benzylideneaceto-1-naphthol. *α -Bromonaphthaflavanone* separates from alcohol in crystals with a cauliflower-like appearance and melts at 134° .

A. McK.

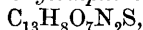
Phenothioxins and Naphthathioxins. FERDINAND MAUTHNER (*Ber.*, 1906, **39**, 1340—1347. Compare *Abstr.*, 1905, i, 461).—The monosodium derivative of *o*-dihydroxydiphenyl disulphide is reduced by

sodium amalgam, neutralised, and a solution of 4-chloro-3:5-dinitrobenzoic acid in ethyl alcohol added. On addition of sodium hydroxide and decomposition of the resulting sodium salt with mineral acid,

4-nitrophenothioxin-2-carboxylic acid, $C_6H_4 \begin{smallmatrix} S \cdot C : C(NO_2) \cdot CH \\ \diagdown \quad \diagup \\ O \cdot C : CH - C \cdot CO_2H \end{smallmatrix}$ is

formed; it separates from glacial acetic acid in orange-red needles and melts at 262° . Its dioxide, $C_{13}H_7O_7NS$, formed by oxidation with chromic acid in glacial acetic acid solution, separates from aqueous methyl alcohol in yellow needles and melts at $296-297^\circ$. The mono-oxide, $C_{13}H_7O_6NS$, formed by oxidation with dilute nitric acid of sp. gr. 1.2, separates from ethyl alcohol in yellow needles and melts at $251-252^\circ$.

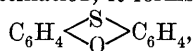
2':4'-Dinitro-2-hydroxydiphenylsulphide-6'-carboxylic acid,



prepared from *o*-dihydroxydiphenyl disulphide, 2-chloro-3:5-dinitrobenzoic acid, and sodium hydroxide, crystallises from xylene in yellow needles and melts at $216-217^\circ$.

4-Aminophenothioxin-2-carboxylic acid, prepared by the reduction of the corresponding nitro-acid with sodium sulphide in alcoholic solution, separates from dilute alcohol in colourless needles and melts and decomposes at 250° . Its salts are completely hydrolysed when boiled with water. Its acetyl derivative separates from alcohol in colourless needles and melts and decomposes at $294-295^\circ$.

Phenothioxin-2-carboxylic acid, $C_6H_4 \begin{smallmatrix} S \cdot C : CH \cdot CH \\ \diagdown \quad \diagup \\ O \cdot C : CH \cdot C \cdot CO_2H \end{smallmatrix}$ prepared by eliminating the amino-group from 4-aminophenothioxin-2-carboxylic acid by the diazo-reaction, crystallises in colourless needles and melts at 223° . Its solution in concentrated sulphuric acid is red, but becomes colourless on the addition of water. When its calcium salt is submitted to dry distillation, it forms phenothioxin,



which separates from alcohol in colourless needles and melts at $60-61^\circ$; its solution in concentrated sulphuric acid is violet. Its dioxide, $C_6H_4 \begin{smallmatrix} SO_2 \\ \diagdown \quad \diagup \\ O \end{smallmatrix} C_6H_4$, prepared by oxidising it with chromic acid in glacial acetic acid solution, separates from a mixture of benzene and light petroleum in colourless needles and melts at $140-141^\circ$. Its solution in concentrated acid is blue and becomes colourless on the addition of water.

Naphthathioxin, $C_{10}H_6 \begin{smallmatrix} S \\ \diagdown \quad \diagup \\ O \end{smallmatrix} C_{10}H_6$, prepared by the action of phosphorus oxychloride on β -dihydroxy- α -dinaphthyl sulphide, separates from glacial acetic acid in yellow needles and melts at $165-166^\circ$. Its solution in warm concentrated sulphuric acid is violet, and on dilution with water becomes colourless. Its oxide, $C_{20}H_{12}O_2S$, prepared by oxidising it with chromic acid in glacial acetic acid solution, forms reddish-yellow needles which melt and decompose at 220° . Its solution in concentrated sulphuric acid is green and becomes colourless on the addition of water.

A. MCK.

Morphine. VII. Conversion of Thebaine into Codeinone and Codeine. LUDWIG KNORR and HEINRICH HÜRLEIN (*Ber.*, 1906, **39**, 1409—1414. Compare *Abstr.*, 1903, i, 849).—When thebaine is hydrolysed by normal sulphuric acid for six to seven minutes at the boiling point or for seventeen days at the ordinary temperature, codeinone is obtained in small quantities. It is detected by its characteristic behaviour during fusion, and in the form of the oxime (*loc. cit.*). C. S.

Degradation of Hydroxycodeine by Exhaustive Methylation. LUDWIG KNORR and WILHELM SCHNEIDER (*Ber.*, 1906, **39**, 1414—1420).—Hydroxycodeine forms a *picrate*, $C_{18}H_{21}O_4N, C_6H_3O_7N_3$, which sinters and melts at 166° , and a *picrolonate*, $C_{18}H_{21}O_4N, C_{10}H_8O_5N_4$, which turns brown at 170° and melts and decomposes at 176° .

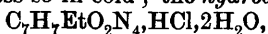
Hydroxymethylmorphimethine, $C_{19}H_{23}O_4N$, obtained by the action of sodium hydroxide on a boiling aqueous solution of hydroxycodeine methiodide, separates as a viscous oil, and, after purification from ether, forms long, colourless, glassy needles containing 1 mol. of the solvent, which is lost between 50° and 60° , the syrup being regenerated. The *hydrochloride*, $C_{19}H_{23}O_4N, HCl$, separates from alcohol in long needles containing alcohol of crystallisation, and, when dried, melts and decomposes at 246° . The *picrate* melts at 211° ; the *picrolonate* sinters at 140° and melts indefinitely. The *methiodide* crystallises from water in needles containing $1\frac{1}{4}H_2O$, and decomposes when anhydrous at 220° . The *di-acetate* melts indefinitely at 81° and forms a *methiodide*, which decomposes at 260° . A 10 per cent. alcoholic potash solution at 100° converts hydroxymethylmorphimethine into a base, which melts indefinitely at 130° and yields a methiodide decomposing at about 300° . From these properties, the base appears to be β -methylmorphimethine (*Abstr.*, 1902, i, 817).

Hydroxymethylmorphimethine decomposes when heated with acetic anhydride, yielding ethanoldimethylamine and a *trihydroxydiacetylmethylphenanthrene*, $C_{19}H_{16}O_5$, which separates from alcohol in needles, melts at 201° , and is therefore not identical with the isomeride obtained from codeinone. C. S.

Action of Xanthine Leucomaines [Ptomaines] on Copper. N. SLOMNESCO (*Compt. rend.*, 1906, **142**, 789—790).—Theobromine, theophylline, or carbamide precipitates the yellow hydroxide of copper from solutions of the salts, and the author is of opinion that this property of the xanthine bases of the organism renders small quantities of copper non-toxic. M. A. W.

Xanthine Bases. ERNST SCHMIDT [and W. SCHWABE] (*Chem. Centr.*, 1906, i, 1241—1242; from *Apoth. Zeit.*, **21**, 213—214. Compare Bergell and Richter, *Abstr.*, 1905, ii, 744).—Most of the following alkyltheophyllines were prepared from potassiumtheophylline in presence of alcohol, but a few were obtained by the action of the alkyl iodide on silvertheophylline. *Ethyltheophylline*, $C_7H_7EtO_2N_4$,

crystallises in white needles, melts at 154° , and is readily soluble in hot water, but somewhat less so in cold; the *hydrochloride*,



the *hydrobromide*, and the *sulphate* form white needles and are decomposed by water. The *aurichloride*, $\text{C}_7\text{H}_7\text{EtO}_2\text{N}_4\cdot\text{HAuCl}_4\cdot\text{H}_2\text{O}$, crystallises in yellow needles and melts at 224° ; the *platinichloride* forms reddish-yellow plates and melts at about 274° . Compounds are also formed with mercuric chloride, mercuric cyanide, silver nitrate, methyl chloride, and methyl iodide, but attempts to prepare an ethiodide failed.

Propyltheophylline and *isopropyltheophylline* crystallise in needles and are readily soluble in water; they melt at $99\text{--}100^{\circ}$ and 140° respectively. *Benzyltheophylline* crystallises in white needles which resemble those of caffeine; it melts at 158° and is very sparingly soluble in water. The *aurichloride* forms yellow needles and melts at 104° ; the *platinichloride* forms reddish-yellow needles and melts about 250° .

E. W. W.

Compound of Lithium with Theobromine. ERNEST DUMESNIL (*J. Pharm. Chim.*, 1906, [vi], 23, 326—328).—A soluble lithium-theobromine compound is obtained by adding an excess of theobromine to a solution of lithium oxide, filtering the mixture, and evaporating the filtrate under reduced pressure over sulphuric acid. The residue is afterwards dried at 110° under reduced pressure. The product obtained has a composition corresponding with the formula $\text{C}_7\text{H}_7\text{O}_2\text{N}_4\text{Li}$, the lithium replacing one hydrogen atom in the theobromine molecule. Lithium-theobromine forms fine needle-like crystals and is soluble in less than half its own weight of water. The solution becomes turbid on exposure to the air owing to the formation of lithium carbonate and free theobromine.

W. P. S.

Dichlorotetrapyridinecobalt Salts. ALFRED WERNER and RUDOLF FEENSTRA (*Ber.*, 1906, 39, 1538—1545).—Dichlorotetrapyridinecobalt salts are formed by the action of aqueous pyridine on dichlorodiaquodiamminecobalt hydrogen sulphate, or, better, by oxidation with chlorine of cobalt chloride dissolved in aqueous pyridine solution. The salts are mostly greyish-green, but the bromide is an intense leaf-green, and the aurichloride is yellowish-green. The chlorine atoms of the dichlorotetrapyridinecobalt nucleus are not removed by prolonged treatment with water at the ordinary temperature, and cannot be substituted by nitrito- or thiocyno-groups. The action of ammonia on the salts leads to the formation of chloropenta-amminecobalt chloride; when boiled with hydrochloric acid, the dichlorotetrapyridinecobalt salts yield cobaltous chloride.

Dichlorodiaquodiamminecobalt hydrogen sulphate is prepared best by the action of sulphuric acid on a cooled aqueous solution of dichlorodiaquodiamminecobalt chloride, which is formed by the action of chlorine on ammonium tetranitritodiamminecobalt dissolved in concentrated hydrochloric acid, cooled by ice.

Dichlorotetrapyridinecobalt chloride, $[\text{Cl}_2\text{CoPy}_4]\text{Cl}\cdot 6\text{H}_2\text{O}$, crystallises in shimmering leaflets, is bluish-green when anhydrous, and in 5 per

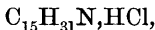
cent. solution gives with potassium cobalticyanide a light green, crystalline precipitate which becomes red, with potassium dichromate a yellowish-brown, and with potassium ferrocyanide an emerald-green coloration, and with sodium nitroprusside a light green crystalline, with iron-alum a dirty-green, and with Erdmann's salt a yellowish-green precipitate. The *bromide*, $[\text{Cl}_2\text{CoPy}_4]\text{Br}$, formed by the action of potassium bromide on the chloride in aqueous solution, separates in small, glistening crystals, or from alcohol in light yellow needles. The *iodide* is obtained as a flocculent, brown precipitate which, when dried, decomposes with separation of iodine; the *thiocyanate* is unstable; the *nitrate*, $[\text{Cl}_2\text{CoPy}_4]\text{NO}_3 \cdot \text{H}_2\text{O}$, crystallises in slender needles; the *hydrogen sulphate*, $[\text{Cl}_2\text{CoPy}_4]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$, forms small leaflets and needles; the *platinichloride*, $[\text{Cl}_2\text{CoPy}_4]_2\text{PtCl}_6$, and the *aurichloride*, $[\text{Cl}_2\text{CoPy}_4]\text{AuCl}_4$, are obtained as crystalline precipitates. G. Y.

Synthesis of Pyridine Bases from Saturated Aldehydes and Ammonia. ALEXEI E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 1229—1253).—The author first discusses the work previously published on this subject, some of which he has repeated. His results show that, in all the cases investigated by him, the action of ammonia on aldehydes consists of a trimolecular condensation proceeding according to the equation:

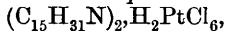


The structure of the compounds formed is similar to that ascribed by Dürkopf and Schlaugk (Abstr., 1888, 607) to the parvoline obtained by Waage (Abstr., 1888, 39; 1884, 172) by the interaction of propaldehyde and ammonia. Acetaldehyde and ammonia yield, besides aldehydecollidine, a small quantity of α -picoline.

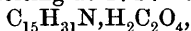
The action of ammonia on *isovaleraldehyde* yields 3:5-diisopropyl-2-isobutylpyridine, to which Ijubavin (Abstr., 1873, 1023) gave the name valeritrine (compare Wischnegradsky, Abstr., 1880, 269). This is an extremely hygroscopic base boiling at 258—259° under 740 mm. pressure, and has the sp. gr. 0.8833 at 20°/0°, 0.8910 at 10°/0°, and 0.8981 at 0°/0°; its hydrochloride melts at 82° and its picrate at 133°. On reduction with sodium and alcohol, it yields *hexahydrovaleritrine*, $\text{C}_{15}\text{H}_{31}\text{N}$, which is a syrupy secondary base boiling at 265° and having sp. gr. 0.8556 at 20°/0°, 0.8625 at 10°/0°, and 0.8694 at 0°/0°; it rapidly absorbs carbon dioxide from the air. The *hydrochloride*,



forms hexagonal needles melting at 286° and dissolves in alcohol or ether, and sparingly in water. The *platinichloride*,



crystallises in microscopic, orange prisms melting and decomposing at 203°. The *picrate*, $\text{C}_{15}\text{H}_{31}\text{N} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{OH}$, crystallises from alcohol in small, shining prisms melting at 174°. The *acid oxalate*,



separates in needles melting and decomposing at 225°. Oxidation of valeritrine by means of potassium permanganate yields pyridine-carboxylic acids.

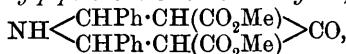
Ljubavin's hydrovaleritrine (*loc. cit.*) is either identical or isomeric with hexahydrovaleritrine.

The action of ammonia on *isovaleraldehyde* yields also a dimolecular condensation product, $C_{15}H_{27}N$, which is a tertiary base boiling at $170-175^\circ$ under 25 mm. pressure; it was not obtained pure and yields no crystalline salts.

The interaction of ammonia and butyraldehyde gives rise to the formation of 3:5-diethyl-2-propylpyridine, $C_{12}H_{19}N$, which is a colourless oil boiling at 242° under 745 mm. pressure and has sp. gr. 0.9141 at $0/0^\circ$ and 0.9042 at $20/0^\circ$. This base is formed by the condensation of 3 mols. of the aldehyde with 1 mol. of ammonia, and probably forms one constituent of Schiff's paradiconiine (Abstr., 1872, 416), which is most likely a mixture. On oxidising the base with potassium permanganate, it yields pyridine-2:3:5-tricarboxylic acid. T. H. P.

Condensation of Acetonedicarboxylic Esters with Benzaldehyde in the Presence of Ammonia. PAVEL I. PETRENKO-KRITSCHENKO and N. ZONEFF (*Ber.*, 1906, 39, 1358-1361. Compare Abstr., 1900, i, 307).—The compounds previously described as substituted tetrahydropyrones are really derivatives of 4-piperidone.

Methyl-2:6-diphenylpiperidone-3:5-dicarboxylate,



obtained by saturating an ice-cold mixture of benzaldehyde (2 mols.) and methyl acetonedicarboxylate (1 mol.) with dry ammonia, melts at $144-148^\circ$ and develops an intense red coloration with ferric chloride. The *nitroso*-derivative, $C_{21}H_{20}O_5N \cdot NO$, melts at $148-149^\circ$. The *hydrochloride*, $C_{21}H_{21}O_5N \cdot HCl$, is precipitated in 80 per cent. yield when hydrogen chloride is passed into a benzene solution of the ester.

Ethyl 2:6-diphenylpiperidone-3:5-dicarboxylate, $C_{23}H_{25}O_5N$, melts at $116-119^\circ$, and the *nitroso*-derivative at $147-150^\circ$; both give a red coloration with ferric chloride. The *hydrochloride*, $C_{23}H_{25}O_5N \cdot HCl$, was also prepared.

A crystalline *potassium* derivative of the ethyl or of the methyl ester can be obtained most conveniently by the addition of alcoholic potassium hydroxide to a cold alcoholic solution of the ester, and is reconverted by boiling water into its generators. C. S.

Constitution of the Indoline Base formed from the *p*-Tolyl-hydrazone of Methyl *iso*Propyl Ketone. ARTHUR KONSCHEGG (*Monatsh.*, 1906, 27, 247-253. Compare Abstr., 1905, i, 924; Plancher, Abstr., 1898, i, 536; Plangger, Abstr., 1905, i, 718).—The acetyl derivative of 3:3:5-trimethyl-2-methyleneindoline is formed by the action of acetyl chloride on the base in presence of sodium acetate; it melts at 104° and is readily hydrolysed by aqueous alkali hydroxides.

The action of methyl iodide on 3:3:5-trimethyl-2-methyleneindoline in boiling methyl-alcoholic solution leads to the formation of a mixture of secondary and tertiary iodides, which crystallises in yellow prisms and melts at 229° . 2:3:3:5-Tetramethyl-*ψ*-indole methiodide,

$\text{C}_6\text{H}_5\text{Me} \left\langle \begin{smallmatrix} \text{CMe}_2 \\ \text{N(MeI)} \end{smallmatrix} \right\rangle \text{CMe}$, which is thrown down on addition of ether to an alcoholic solution of the mixed iodides, crystallises in glistening, silky, slightly yellow needles and melts at 228° . 1:3:3:5-Tetramethyl-2-methyleneindoline, $\text{C}_6\text{H}_5\text{Me} \left\langle \begin{smallmatrix} \text{CMe}_2 \\ \text{NMe} \end{smallmatrix} \right\rangle \text{C:CH}_2$, is formed by the action of potassium hydroxide on the methiodide; it is a colourless oil, which distils at 134° under 10 mm. pressure, becomes red on exposure to air, and forms a *ferrichloride* and a *platinichloride*. The *picrate* crystallises in transparent, yellow plates and melts at 122° . G. Y.

Constitution of Thiazine and Oxazine Dyes. ARTHUR HANTZSCH (*Ber.*, 1906, 39, 1365—1366. Compare this vol., i, 206).—A reply to Kehrman (this vol., i, 306). C. S.

Conversion of Hydrazine Derivatives into Heterocyclic Compounds. XIX. Diacyldihydrazide Dichlorides. ROBERT STOLLÉ (*J. pr. Chem.*, 1906, [ii], 73, 277—287. Compare Abstr., 1905, i, 249).—A *résumé* of the methods of preparing diacyldihydrazide dichlorides, $\text{R}\cdot\text{CCl}\cdot\text{N}\cdot\text{N}\cdot\text{CCl}\cdot\text{R}$, and of their conversion into heterocyclic compounds. G. Y.

Oxidation of Diphenylamine. HEINRICH WIELAND and STEPHAN GAMBARJAN (*Ber.*, 1906, 39, 1499—1506. Compare Wieland, Abstr., 1903, ii, 685; Baeyer, Abstr., 1905, i, 281).—Tetraphenylhydrazine is formed by the oxidation of diphenylamine with lead peroxide in benzene, or potassium permanganate in acetone solution. When treated with concentrated sulphuric, aqueous, hydrochloric, or acetic acid, it is hydrolysed to diphenylamine and the salt of the hypothetical diphenylhydroxylamine, which is the source of the blue or violet coloration. If treated with hydrogen chloride in anhydrous ethereal solution, it gives an intense dark green coloration, which rapidly fades, and the resulting solution, after depositing diphenylaminehydrochloride, contains *p*-chlorodiphenylamine the product of isomeric change of diphenylhydroxylamine chloride. Tetraphenylhydrazine reacts in the same manner with hydrogen bromide.

Tetra-*p*-tolylhydrazine is formed by the oxidation of di-*p*-tolylamine with lead dioxide in benzene solution. With glacial acetic acid, it gives a more intense coloration than does tetraphenylhydrazine, and when treated with hydrogen chloride in ethereal solution cooled by ice gives a deep reddish-violet coloration, which fades only very slowly, di-*p*-tolylamine hydrochloride crystallising out. The coloured substance can be isolated as the *stannichloride*, which forms large, dark red crystals, and is decolorised rapidly on treatment with water; the ethereal solution gives intense colorations with acids.

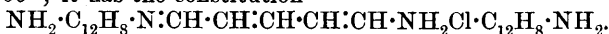
When fused with phenol, tetraphenylhydrazine forms diphenylamine and a colourless compound (triphenylamine?), no colour change being observed. Diphenylamine is formed also by reduction of tetraphenylhydrazine with zinc dust and glacial acetic acid.

Diphenylbenzidine (Kadiera, Abstr., 1905, i, 934) is formed together

with the blue diphenylhydroxylamine sulphate by the action of concentrated sulphuric acid on tetraphenylhydrazine.

The action of concentrated sulphuric acid on a mixture of diphenylamine and *p*-hydroxydiphenylamine leads to the formation of 4-*hydroxydiphenylamine-3-sulphonic acid*, $\text{NHPh}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{SO}_3\text{H}$, which crystallises in glistening scales, melts and decomposes at $290\text{--}291^\circ$, is insoluble in alcohol, gives an intense red coloration with ferric chloride, potassium dichromate, or permanganate in aqueous solution, and reduces silver nitrate and Fehling's solutions (compare Limpricht, Abstr., 1889, 397). G. Y.

Action of Pyridine on 1:5-Dichloro-2:4-dinitrobenzene. FRITZ REITZENSTEIN and JULIUS ROTHSCILD (*J. pr. Chem.*, 1906, [ii], 73, 257—276. Compare Reitzenstein, Abstr., 1903, i, 815; Zincke, Abstr., 1904, i, 448; 1905, i, 467; König, Abstr., 1904, i, 449, 817).—The moss-green compound, formed together with 2:4-dinitroaniline by the action of dinitrophenylpyridinium chloride on benzidine (Reitzenstein, *loc. cit.*), is found now to melt at $159\text{--}160^\circ$; it has the constitution



The action of an excess of pyridine and 1-chloro-2:4-dinitrobenzene on aniline in alcoholic solution leads to the formation of the hydrochloride of the dianilide melting at 143° (Zincke, Heuser, and Möller, Abstr., 1904, i, 921), dinitrodiphenylamine melting at 155° , and dinitroaniline melting at $181\text{--}183^\circ$.

Dinitroaniline and dinitrophenylbenzidine, melting at 245° , are formed by the action of an excess of pyridine and 1-chloro-2:4-dinitrobenzene on benzidine in alcohol.

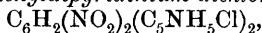
The red *dianilide*,

$\text{NH}_2\cdot\text{C}_{12}\text{H}_6(\text{SO}_3\text{H})_2\cdot\text{N}:\text{CH}:[\text{CH}:\text{CH}]_2\cdot\text{NH}_2\text{Cl}\cdot\text{C}_{12}\text{H}_8(\text{SO}_3\text{H})_2\cdot\text{NH}_2\cdot\text{H}_2\text{O}$, is formed by the action of dinitrophenylpyridinium chloride on benzdinedi-*m*-sulphonic acid; it melts above 270° and does not dye wool or mordanted cotton-wool either in aqueous or alkaline solution.

The green *dianilide*,

$\text{NH}_2\cdot\text{C}_{12}\text{H}_7(\text{SO}_3\text{H})\cdot\text{N}:\text{CH}:\text{CH}:\text{CH}:\text{CH}:\text{CH}:\text{NH}_2\text{Cl}\cdot\text{C}_{12}\text{H}_7(\text{SO}_3\text{H})\cdot\text{NH}_2$, formed from benzidinesulphonic acid and dinitrophenylpyridinium chloride, melts at $245\text{--}255^\circ$.

The action of pyridine on 1:5-dichloro-2:4-dinitrobenzene leads to the formation of (a) the greenish-yellow condensation product, $\text{C}_6\text{H}_2(\text{NO}_2)_2 \left\langle \begin{smallmatrix} \text{C}_5\text{NH}_5\cdot\text{O} \\ \text{C}_5\text{NH}_5\cdot\text{O} \end{smallmatrix} \right\rangle \text{C}_6\text{H}_2(\text{NO}_2)_2$, which melts above 300° , dissolves in aniline or alkali hydroxides, and is readily soluble in dilute acids, and (b) *dinitrophenyldipyridinium dichloride*,



which crystallises from alcohol, melts at $147\text{--}148^\circ$, gives a green precipitate with sodium hydroxide, becoming reddish-brown on addition of acids, and when boiled with pyridine is converted into the condensation product.

When boiled with hydrochloric acid, the condensation product is decomposed, forming 2:4-dinitro-5-hydroxyphenylpyridinium hydroxide, $\text{OH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{C}_5\text{NH}_5\cdot\text{OH}$, which is obtained in glistening,

red crystals melting at 208°. The yellow isomeric *additive* compound of pyridine and dinitroresorcinol, $C_6H_2(NO_2)(OH)_2.C_5NH_5$, melts at 111° and is decomposed into its components on treatment with dilute sodium hydroxide.

When heated on the water-bath with aniline in alcoholic solution, dinitrophenyldipyridinium dichloride forms the hydrochloride of the dianilide melting at 143° (Zincke, Heuser, and Müller, *loc. cit.*), together with 4:6-dinitro-1:3-diaminobenzene, $C_6H_2(NH_2)_2(NO_2)_2$, which separates in yellow crystals, melts above 300°, and is soluble in ethyl acetate.

With benzidine, benzidinedi-*m*-sulphonic acid, 4:4'-tetramethyldiamino-3''-amino-5''-methyltriphenylmethane, and 4:4'-tetramethyldiamino-3''-amino-2:2':5''-trimethyltriphenylmethane, dinitrophenyldipyridinium dichloride yields the same dianilides, melting at 159–160°, above 270°, 115°, and 113° respectively, as are formed by dinitrophenylpyridinium chloride.

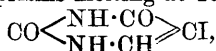
G. Y.

Action of Hippuryl Chloride on 2-Methylindole. EMIL FISCHER and CARL KAAS (*Ber.*, 1906, 39, 1276–1278).—3-Hippuryl-2-methylindole, $COPh \cdot NH \cdot CH_2 \cdot CO \cdot C \begin{smallmatrix} \text{CMe} \\ \text{C}_6\text{H}_4 \end{smallmatrix} > NH$, is formed when an intimate mixture of 2-methylindole, hippuryl chloride, and magnesium oxide is heated with dry benzene at 60–70°, while the whole is well shaken. It remains undissolved when the residue after filtration is extracted first with ether and then with dilute hydrochloric acid. It may be crystallised from glacial acetic acid or from alcohol, although only sparingly soluble in the latter. It begins to turn brown at 250°, melts and decomposes at about 269° (corr.), and dissolves sparingly in the ordinary organic solvents with the exception of glacial acetic acid.

When hydrolysed by heating at 100° with glacial acetic acid saturated with hydrogen chloride at 0°, it yields 3-aminoacetyl-2-methylindole (3-glycyl-2-methylindole), $NH_2 \cdot CH_2 \cdot CO \cdot C \begin{smallmatrix} \text{CMe} \\ \text{C}_6\text{H}_4 \end{smallmatrix} > NH$, together with a complex compound melting at 190°. The glycyl compound forms small, colourless needles which, when moist, rapidly darken in contact with air. When rapidly heated, it melts and decomposes at 176° (corr.) and dissolves readily in dilute acids or in hot water, but only sparingly in warm benzene or toluene. It readily reduces Fehling's solution.

J. J. S.

Derivatives of 5-Iodopyrimidine: 5-Iodocytosine. TREAT B. JOHNSON and CARL O. JOHNS (*J. Biol. Chem.*, 1906, 1, 305–318).—5-Iodo-6-oxy-2-ethylthiopyrimidine, $SEt \cdot C \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{N} - \text{CH} \end{smallmatrix} > Cl$, obtained by the action of an alkaline solution of iodine on 6-oxy-2-ethylthiopyrimidine (Wheeler and Merriam, *Abstr.*, 1903, i, 525), crystallises from alcohol in slender prisms melting at 196°. 5-Iodouracil,



obtained from uracil in a similar manner, crystallises from water in glistening scales and decomposes at 272° .

5-Iodocytosine, $\text{CO} \begin{smallmatrix} \text{N}:\text{C}(\text{NH}_2) \\ \text{NH}-\text{CH} \end{smallmatrix} \text{Cl}$, decomposes between 225° and 245° , evolving iodine. It is practically insoluble in alcohol or benzene, and its solubility in water is somewhat less than 1 in 1000. The *picrate*, $\text{C}_4\text{H}_4\text{ON}_3\text{I} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, crystallises from hot water in long needles and decomposes between 247° and 257° . The *acetate* decomposes at $220-240^{\circ}$ and dissociates when warmed with acetic acid.

6-Chloro-5-iodo-2-ethylthiopyrimidine, $\text{SEt} \cdot \text{C} \begin{smallmatrix} \text{N}:\text{CCl} \\ \text{N}-\text{CH} \end{smallmatrix}$, obtained by the action of phosphorus oxychloride on the 5-iodo-derivative, crystallises from light petroleum in large prisms melting at 69° , and when heated with an alcoholic solution of ammonia at $128-130^{\circ}$ yields 5-iodo-6-amino-2-ethylthiopyrimidine, $\text{C}_6\text{H}_8\text{N}_3\text{SI}$, which crystallises from alcohol in slender prisms melting at 127° . When boiled with concentrated hydrochloric acid, the amino-compound is transformed quantitatively into 5-iodocytosine. 5-Iodo-6-anilino-2-ethylthiopyrimidine is an oil, but yields a crystalline *sulphate*, $(\text{C}_{12}\text{H}_{12}\text{N}_3\text{SI})_2 \cdot \text{H}_2\text{SO}_4$.

6-Oxy-2-anilinopyrimidine, $\text{NHPh} \cdot \text{C} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{N}-\text{CH} \end{smallmatrix}$, obtained by warming 6-oxy-2-ethylthiopyrimidine with the theoretical amount of aniline or by the action of aniline on 5-iodo-6-oxy-2-ethylthiopyrimidine, crystallises from alcohol in well-developed plates, melts at $230-231^{\circ}$, and is insoluble in water or benzene. Ammonium hydroxide solution reacts in much the same manner as aniline and converts the iodo-derivative into 2-amino-6-oxypyrimidine, whereas alcoholic ammonia has no action. Aniline does not react with 5-iodo-6-amino-2-ethylthiopyrimidine or with 5-iodocytosine. Alcoholic ammonia converts 5-iodocytosine into cytosine, and 5-iodouracil into uracil.

α -Cyanobutrylcarbamide, $\text{CN} \cdot \text{CHEt} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, obtained by condensing α -cyanobutyric acid with carbamide, crystallises from water and melts at 181° with slight evolution of gas. When its solution in concentrated sodium hydroxide is kept for some hours and then neutralised with hydrochloric acid, 6-amino-2:4-dioxy-5-ethylpyrimidine, $\text{CO} \begin{smallmatrix} \text{N}:\text{C}(\text{NH}_2) \\ \text{NH}-\text{CO} \end{smallmatrix} \text{CHEt}$, is obtained. It crystallises from water in acicular prisms and decomposes at 339° .

The iodine atoms in the compounds described are firmly united to carbon, and the compounds do not react with the potassium salt of phthalimide or the sodium salt of urethane. J. J. S.

Preparation of Guanine. EMANUEL MERCK (D.R.-P. 162336).—2-Cyanoamino-4-amino-6-hydroxypyrimidine (Abstr., 1905, i, 670) forms an *isonitroso*-derivative, which, on reduction, yields yellow needles of 2-cyanoamino-4:5-diamino-6-hydroxypyrimidine. When heated with 90 per cent. formic acid, the formate of the base at first crystallises out, but on boiling for several hours is converted into guanine formate, which may be decomposed by sodium hydroxide, yielding the base. C. H. D.

Stereochemistry of the 2:5-Diketopiperazines. EMIL FISCHER and KARL RASKE (*Sitzungsber. K. Akad. Wiss. Berlin*, 1906, 371—383).—The A-isomeride of α -aminobutyryl- α -aminobutyric acid melts at 272—275° (corr.) under elimination of water and formation of an anhydride; it crystallises in glistening leaflets and forms a sparingly soluble copper salt; 5.4 grams of the acid dissolve in 100 grams of water at 24°. The B-isomeride melts at 260—262° (corr.), crystallises in short, obliquely cut, prismatic needles, and forms a soluble copper salt; 29 grams of the acid dissolve in 100 grams of water. On esterification and treatment with alcoholic ammonia, both isomerides are converted into anhydrides. A-diketodiethylpiperazine crystallises in long, narrow, obliquely cut plates aggregated in clusters, and melts at 277—278° (corr.) to a faintly brown liquid; 0.33 gram dissolves in 100 grams of water; the B-isomeride crystallises in thin, obliquely cut prisms generally badly formed, and melts to a faint brown liquid at 266—267° (corr.); 100 grams of water dissolve 1.03 grams of the acid. The anhydride formerly prepared by heating either the A- or B-dipeptides melts at 268—269° (corr.) and is regarded as a mixture.

Both A- and B-diketodiethylpiperazines when hydrolysed with alkali are converted into a dipeptide crystallising in small glistening plates, melting at 274—275° (corr.), forming a sparingly soluble copper salt, and dissolving in water to the extent of 5.2 grams per 100 grams of water.

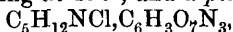
l-Bromopropionyl-*d*-alanine, obtained by condensing *d*-alanine with *l*-bromopropionyl chloride in presence of cold sodium hydroxide, melts and decomposes at 165°, and has $[\alpha]_D$ between -60.4° and -63.6° . *l*-Alanyl-*d*-alanine, $\text{NH}_2\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, prepared by hydrolysing bromopropionylalanine with aqueous ammonia, crystallises in small plates with lancet ends, often in stellate aggregates. It melts at 269—270° (corr.) to a faintly yellow liquid, and has $[\alpha]_D -68.5^\circ$ at 20°. *trans*-Alanine anhydride, obtained by conversion of *l*-alanyl-*d*-alanine into the ester and acting on this with alcoholic ammonia, crystallises in thin, hexagonal, rhombic plates melting at 277—278° (corr.) to a yellow liquid. It is optically inactive and yields an inactive dipeptide on hydrolysis. E. F. A.

Synthesis and Degradation of an Octocyclic Nuclear-homologue of 1:4-Dimethylpiperazine Dimethochloride. LUDWIG KNORR and PAUL ROTH (*Ber.*, 1906, 39, 1420—1429. Compare Abstr., 1904, i, 938; 1905, i, 834).—Dimethyl- γ -chloropropylamine is relatively stable, but on keeping for a month either alone or in aqueous solution it polymerises into *N*-dimethylbistrimethylenedimine dimethochloride. The same change occurs in a day at 100°, and in fifteen hours at 150°. The polymeride is decomposed by a boiling solution of potassium hydroxide, yielding dimethylallylamine, tetramethyltrimethylenediamine, and a substance, $\text{C}_8\text{H}_{10}\text{O}$, which is probably isovalyl ether, $\text{O}(\text{CMe}\cdot\text{CH}_2)_2$.

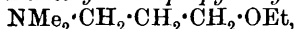
The following new compounds are described.

Phenyl γ -dimethylaminopropyl ether, $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OPh}$, obtained by heating an alcoholic solution of phenyl γ -bromopropyl ether

(Lohmann, Abstr., 1891, 1467) and dimethylamine for four hours at 150°, is a colourless oil, which boils at 249—250° under 756 mm. pressure and has a faint ammoniacal odour. The *picrate* melts at 118—119°. When heated with concentrated hydrochloric acid at 170—180°, the substance yields *dimethyl-γ-chloropropylamine hydrochloride*, which crystallises with difficulty and forms an *aurichloride*, $C_5H_{12}NCl, HAuCl_4$, melting at 150°, and a *picrate*,

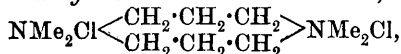


which melts at 110°. The *base*, $CH_2Cl \cdot CH_2 \cdot CH_2 \cdot NMe_2$, is a colourless oil with a strong ammoniacal odour and boils at 134—135° under 765 mm. pressure. *γ-Dimethylaminopropyl ethyl ether*,



obtained from the base and sodium ethoxide at 150°, is a colourless oil with an ammoniacal odour and boils at 144° under 749 mm. pressure. The *aurichloride*, $C_7H_{17}ON, HAuCl_4$, melts at 70—71°.

N-Dimethylbistrimethylenedi-imine dimethochloride,

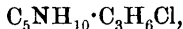


is a colourless, hygroscopic substance soluble in water, insoluble in alcohol. The *aurichloride*, $(C_5H_{12}N, AuCl_4)_2$, melts and decomposes at 247—248°. The *platinichloride*, $(C_5H_{12}N)_2PtCl_6$, decomposes at 275—276°.

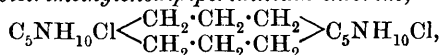
Dimethylallylamine, $C_5H_{11}N$, a decomposition product of the preceding cyclic compound, was also prepared from allyl iodide and an alcoholic solution of dimethylamine at 150°. It boils at 64° under 743 mm. pressure, has a strong ammoniacal odour, dissolves in water, alcohol, or ether, and forms a *picrate* which melts at 95°.

Tetramethyltrimethylenediamine, $NMe_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NMe_2$, another decomposition product, was also prepared from *αγ*-dibromopropane and alcoholic dimethylamine at 150°. It boils at 145—146° under 755 mm. pressure and forms a *picrate*, $C_7H_{18}N_2, 2C_6H_3O_7N_3$, which sinters and melts at 205°. The *platinichloride*, $C_7H_{18}N_2, H_2PtCl_6$, decomposes at 246—247°. C. S.

Formation of an Octocyclic Polymeride from *γ*-Chloropropylpiperidine. HEINRICH HÖRLEIN and RUDOLF KNEISEL (*Ber.*, 1906, 39, 1429—1435. Compare preceding abstract).—1-*γ*-Chloropropylpiperidine hydrochloride, $C_5NH_{10} \cdot C_3H_6Cl, HCl$, obtained by heating 1-*γ*-phenoxypropylpiperidine (Gabriel and Stelzner, Abstr., 1896, i, 702) and hydrochloric acid at 150° for five hours, crystallises in leaflets, melts at 215—216°, and decomposes at 230°. It can be sublimed in felted, doubly refractive needles. The *base*,



boils at 210° under 742 mm. pressure. The *aurichloride* melts indefinitely at 100°. When the base is heated in aqueous-alcoholic solution until the liquid has only a faint alkaline reaction, a hygroscopic mass of *bistrimethylenedipiperidinium chloride*,

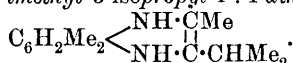


is obtained (compare Gabriel and Stelzner, *loc. cit.*), which is unchanged by hydrochloric acid on the water-bath, is converted by hydrobromic

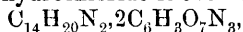
acid into 1- γ -bromopropylpiperidine hydrobromide, and is decomposed by distillation with a 50 per cent. solution of potassium hydroxide into trimethylenedipiperidine (Töhl, Abstr., 1895, i, 681), piperidine, allylpiperidine, and a substance which is probably isoallyl ether.

C. S.

A Second 1:4-Dihydroquinoxaline. JOHN B EKELEY (*Ber.*, 1906, 39, 1646—1649. Compare Abstr., 1905, i, 613).—*o*-Xylylene-3:5-diamine, obtained by reducing *o*-nitro-*m*-xylydine with zinc dust and sodium hydroxide solution, readily condenses with mesityl oxide in the presence of dry hydrogen chloride, yielding the hydrochloride of 2:6:8-trimethyl-3-isopropyl-1:4-dihydroquinoxaline,



The base crystallises from dilute acetone in brown needles melting at 82—83°, and dissolves readily in organic solvents and in dilute acids. The *hydrochloride*, $\text{C}_{14}\text{H}_{20}\text{N}_2 \cdot 2\text{HCl}$, obtained by passing hydrogen chloride into an ethereal solution of the base, forms a colourless, crystalline precipitate. A yellow *monohydrochloride* also exists. Similar *hydrobromides* and *hydroiodides* have been prepared. When hydrogen chloride is led into a chloroform solution of the base, a colloidal solution of the hydrochloride is obtained. The *picrate*,



forms glistening, yellow needles.

J. J. S.

Quinacridone. FRITZ ULLMANN and RUDOLF MAAG (*Ber.*, 1906, 39, 1693—1696).—The interaction, for two and a half hours at 140—150°, of anthranilic acid, *p*-dibromobenzene, and potassium carbonate in the presence of amyl alcohol and small quantities of cuprous chloride and copper dust as catalysts leads to the formation of *p*-phenylenedianthranilic acid, $\text{C}_6\text{H}_4(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_2$, and *p*-bromophenyldianthranilic acid, $\text{C}_6\text{H}_4\text{Br} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$; they are separated by means of the weaker basicity of the former acid, which separates from pyridine in lustrous, faintly green leaflets, darkens at 276°, and melts and decomposes at 286°. The latter crystallises in clusters of yellow needles and melts at 182°.

Quinacridone, $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{C}_6\text{H}_4$, obtained by heating *p*-phenylenedianthranilic acid with concentrated sulphuric acid on the water-bath, crystallises in yellow needles, melts at 394°, and dissolves in concentrated sulphuric acid to a yellow solution with a greenish-blue fluorescence.

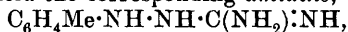
C. S.

Preparation of *m*-Tolylsemicarbazide. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 162630, 162823, 163035, 163036, 163037, and 163038. Compare Abstr., 1905, i, 383, 949).—*m*-Tolylsemicarbazide may be prepared by the action of carbamic chloride, $\text{NH}_2 \cdot \text{COCl}$, on *m*-tolylhydrazine in benzene solution, the product being washed with water to remove *m*-tolylhydrazine hydrochloride and recrystallised.

Phenyl m-tolylhydrazinecarboxylate, $C_6H_4Me \cdot NH \cdot NH \cdot CO_2Ph$, prepared from phenyl chlorocarbonate and *m*-tolylhydrazine, forms colourless crystals and melts at 134° , *methyl m-tolylhydrazinecarboxylate* forms white crystals and melts at 119° . Both esters yield *m*-tolylsemicarbazide when warmed with aqueous ammonia.

Benzaldehyde-m-tolylhydrazone, $CHPh \cdot CH : N \cdot NH \cdot C_6H_4Me$, forms yellowish-white crystals, almost insoluble in water, and melts at 96° . The action of phosgene in benzene solution in the presence of pyridine converts it into the *chloride*, $CHPh \cdot CH : N \cdot N(COCl) \cdot C_6H_4Me$, which forms colourless crystals and melts at $69-70^\circ$. Alcoholic ammonia reacts with the chloride to form *benzaldehyde-2-m-tolylsemicarbazone*, $CHPh \cdot CH : N \cdot N(NH_2) \cdot C_6H_4Me$, which separates from water in colourless crystals and melts at 142° . Heating with dilute alcoholic sulphuric acid hydrolyses it to *2-m-tolylsemicarbazide*, $C_6H_4Me \cdot N(NH_2) \cdot CO \cdot NH_2$, which crystallises in needles and melts at 88° . Heating it to 140° converts it into *m*-tolylsemicarbazide (compare Busch and Walter, Abstr., 1903, i, 522).

m-Tolylhydrazine reacts with cyanogen bromide in ethereal solution, yielding *m-tolylhydrazinonitrile*, $C_6H_4Me \cdot NH \cdot NH \cdot CN$, an easily decomposable oil. Shaking its ethereal solution with dilute hydrochloric acid hydrolyses it to *m*-tolylsemicarbazide. Hydrogen chloride acts on the ethereal solution of the nitrile, giving a white, hygroscopic mass of the *iminochloride*, $C_6H_4Me \cdot NH \cdot NH \cdot CCl : NH$. Cyanamide and *m*-tolylhydrazine yield the corresponding *amidine*,



crystallising from alcohol in leaflets and melting at $190-192^\circ$. Both the iminochloride and the amidine are hydrolysed to *m*-tolylsemicarbazide by bases.

m-Tolylhydrazinonitrile reacts with alcohols and hydrogen haloids in ethereal solution to form *imino-ethers* of *m*-tolylhydrazinecarboxylic acid, $C_6H_4Me \cdot NH : NH \cdot C(OR) : NH \cdot HCl$, which may be hydrolysed to *m*-tolylsemicarbazide.

C. H. D.

Methylene-azure. FRIEDRICH KEHRMANN and A. DUTTENHÖFER (*Ber.*, 1906, 39, 1403—1408).—Methylene-azure, one of the products into which methylene-blue is decomposed by the action either of alkali and air or of silver oxide, has hitherto been regarded as containing oxygen (compare Bernthsen, Abstr., 1886, 53; Fischer and Hepp, Abstr., 1905, i, 948; Hantzsch, this vol., i, 206). The authors show that the two reactions lead to the production of different compounds, which have been isolated and purified in the form of the chlorides. The first reaction gives rise chiefly to *as*-dimethylthionine, the *chloride* of which, $NH_2 \cdot C_6H_3 \cdot \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{SCl} \end{smallmatrix} \gg C_6H_3 \cdot NMe_2$, crystallises in brownish-green needles and is identical with the compound synthesised from dimethylaniline and monoaminophenothiazonium chloride. The decomposition of methylene-blue by silver oxide leads to the formation chiefly of trimethylthionine, the *chloride* of which,



crystallises in metallic-looking green needles very soluble in water, and

is identical with the synthetical compound obtained by the thiosulphate method.

Detailed descriptions are given for the purification of the two compounds. C. S.

CC-Dialkylbarbituric Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 162219. Compare Abstr., 1905, i, 671).—The 4 : 6-dioxy-2-thiodialkylpyrimidines may be oxidised to CC-dialkylbarbituric acids by means of nitric or nitrous acids or hydrogen peroxide, the sulphur being thus removed. The compounds employed as starting point for the reaction are prepared by condensing dialkylated ethyl cyanoacetates with thiocarbamide and hydrolysing the iminothiodi-oxydialkylpyrimidines formed.

Ethyl diethylecyanoacetate condenses with thiocarbamide in presence of sodium ethoxide to form 4-imino-6-oxy-2-thio-5-diethylpyrimidine, $\text{CS}\cdot\text{NH}-\text{CO}$
 $\text{NH}\cdot\text{C}(\text{NH})\text{C}(\text{Et})_2$, which crystallises from hot water in yellow needles, melts at 256°, and dissolves readily in dilute alkali hydroxides.

Warming with 30 per cent. sulphuric acid hydrolyses it to 4 : 6-dioxy-2-thio-5-diethylpyrimidine, which forms pale yellow needles, melts at 182°, and yields diethylbarbituric acid on oxidation.

4-Imino-6-oxy-2-thio-5-dimethylpyrimidine melts at 215° and dissolves sparingly in water or alcohol; 4 : 6-dioxy-2-thio-5-dimethylpyrimidine forms pale yellow needles, melts at 240°, and yields dimethylbarbituric acid on oxidation. C. H. D.

CC-Diethylbarbituric Acid. EMANUEL MERCK (D.R.-P. 162220. Compare Abstr., 1905, i, 751, and preceding abstract).—Biuret, fused with diethylmalonyl chloride at 130°, forms CC-diethylbarbituric acid and cyanuric acid, which may be separated by crystallisation from water: $\text{NH}(\text{CO}\cdot\text{NH}_2)_2 + \text{C}(\text{Et})_2(\text{COCl})_2 \rightarrow \text{NH}_2\cdot\text{CO}\cdot\text{N}-\text{CO}-\text{C}(\text{Et})_2 \rightarrow$
 $\text{NH}-\text{CO}-\text{C}(\text{Et})_2$
 $\text{CO}\cdot\text{NH}\cdot\text{CO}$ C. H. D.

Conversion of Hydrazine Derivatives into Heterocyclic Compounds. XX. Dibenzoylhydrazide Dichloride. ROBERT STOLLÉ and KARL THOMÄ (*J. pr. Chem.*, 1906, [ii], 73, 288—300. Compare preceding abstract).—Dibenzoylhydrazide dichloride, $\text{CClPh}\cdot\text{N}\cdot\text{N}\cdot\text{CClPh}$

(Günther, Abstr., 1889, 1067), is formed together with 2 : 5-diphenyl-1 : 3 : 4-oxadiazole by the action of powdered phosphorus pentachloride on dibenzoylhydrazide at 110°; it crystallises from alcohol in small prisms, melts at 123°, is readily soluble in ether or hot alcohol, does not reduce ammoniacal silver or Fehling's solutions, and is converted into diphenyloxadiazole by boiling with alcoholic silver nitrate or for some time with water. It yields hydrazine hydrochloride when heated with alcoholic hydrogen sulphide at 130° under pressure, 2 : 5-diphenyl-1 : 3 : 4-thiodiazole when heated with phosphorus pentasulphide at 200° in a vacuum, 2 : 5-diphenyl-1 : 3 : 4-triazole and 2 : 5-diphenyl-1 : 3 : 4-oxadiazole when heated with alcoholic ammonia at 180°.

and 1 : 2 : 5-triphenyl-1 : 3 : 4-triazole, melting at 292° (m. p. 304—305° : Pellizzari and Alicatore, Abstr., 1901, i, 571), when heated with aniline at 170°.

2 : 5-Diphenyl-1 : 3 : 4-oxadiazole is formed almost quantitatively by the action of phosphorus oxychloride on dibenzoylhydrazide.

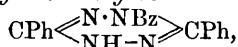
2 : 5-Diphenyl-1-*o*-tolyl-1 : 3 : 4-triazole, $\begin{smallmatrix} \text{N:CPh} \\ \text{N:CPh} \end{smallmatrix} > \text{N} \cdot \text{C}_7\text{H}_7$, formed by heating dibenzoylhydrazide dichloride with *o*-toluidine at 200°, crystallises from alcohol in small scales and melts at 184°; the silver nitrate derivative crystallises in slender needles and melts and decomposes at 278°.

2 : 5-Diphenyl-1-xylyl-1 : 3 : 4-triazole, $\text{C}_{22}\text{H}_{19}\text{N}_3$, crystallises from alcohol in matted, glistening, slender needles, melts at 252°, and gives a white precipitate with silver nitrate in alcoholic solution.

1-Hydroxy-2 : 5-diphenyl-1 : 3 : 4-triazole, $\begin{smallmatrix} \text{N:CPh} \\ \text{N:CPh} \end{smallmatrix} > \text{N} \cdot \text{OH}$, is formed by boiling dibenzoylhydrazide dichloride with hydroxylamine in alcoholic solution in a reflux apparatus. It crystallises from ether in colourless prisms, melts at 185—186°, is soluble in alcohol, ether, benzene, or dilute alkali hydroxides or ammonia, and gives a white precipitate with silver nitrate and ammonia in alcoholic solution.

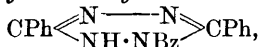
When heated with hydrazine hydrate in alcoholic solution in a reflux apparatus, dibenzoylhydrazide dichloride yields 3 : 6-diphenyl-1 : 2-dihydro-1 : 2 : 4 : 5-tetrazine.

1-Benzoyl-3 : 6-diphenyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine,



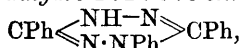
is formed together with dibenzoylhydrazide by heating dibenzoylhydrazide dichloride with benzoyl hydrazide at 130—135°; it separates from alcohol in transparent crystals, melts at 240°, dissolves in alcohol, dilute alkali hydroxides, or ammonia, forms a precipitate with silver nitrate and a small quantity of ammonia, and is hydrolysed by alcoholic-aqueous hydrogen chloride at 130—140° under pressure, forming 3 : 6-diphenyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine.

1-Benzoyl-3 : 6-diphenyl-1 : 2-dihydro-1 : 2 : 4 : 5-tetrazine,



is formed by boiling 3 : 6-diphenyl-1 : 2-dihydro-1 : 2 : 4 : 5-tetrazine with benzoyl chloride in benzene in presence of sodium carbonate in a reflux apparatus. It crystallises from benzene in lemon-yellow needles, melts and decomposes at 208°, and does not reduce Fehling's or ammoniacal silver solutions.

1 : 3 : 6-Triphenyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine,



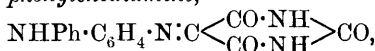
is formed, together with the hydrochloride of the 1 : 2-dihydro-base, by heating dibenzoylhydrazide dichloride with phenylhydrazine in alcoholic solution in a reflux apparatus; it is colourless, melts at 263°, is only slightly soluble in alcohol or dilute acids, reduces Fehling's solution on prolonged boiling, gives a white precipitate with silver nitrate and

ammonia in alcoholic solution, and is converted by nitrous acid into 2:5-diphenyl-1:3:4-triazole.

1:3:6-Triphenyl-1:2-dihydro-1:2:4:5-tetrazine hydrochloride melts at 180°, is readily soluble in water, and is hydrolytically dissociated when boiled with water. The base, $\text{CPh} \begin{smallmatrix} \text{N} \text{---} \text{N} \\ \text{NH} \cdot \text{NPh} \end{smallmatrix} \text{CPh}$, crystallises from alcohol in glistening, golden, slender needles, melts at 126°, and is readily soluble in the ordinary organic solvents. It yields hydrazine when boiled with dilute hydrochloric acid, reduces alcoholic silver nitrate, is converted into diphenyloxadiazole when treated with nitrous acid, and changes into the *s*-isomeride when boiled with alcoholic hydrogen chloride.

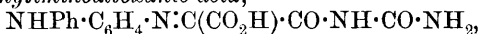
Dibenzoylhydrazide diethyl ether, $\text{OEt} \cdot \text{CPh} \cdot \text{N} \cdot \text{N} \cdot \text{CPh} \cdot \text{OEt}$, formed together with 2:5-diphenyloxadiazole by boiling the dichloride with sodium ethoxide in alcoholic solution in a reflux apparatus, crystallises in colourless octahedra and melts at 83–84°. G. Y.

Condensation Products of *N*-Substituted *o*-Diamines with Alloxan and its Derivatives. OTTO KÜHLING and O. KASELITZ (*Ber.*, 1906, 39, 1314–1326. Compare *Abstr.*, 1893, i, 324).—*Alloxanylphenyl-o-phenylenediamine*,



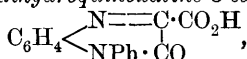
prepared from phenyl-*o*-phenylenediamine and alloxan, separates from glacial acetic acid in yellow crystals and melts at 232°. Its solution in concentrated sulphuric acid is cherry-red; its solution in hydrochloric or nitric acid is reddish-yellow.

Anilinophenyliminoalloxanic acid,



prepared by the action of dilute sodium hydroxide on the preceding compound, separates from a mixture of acetone and light petroleum in tetragonal leaflets and melts at 228°.

2-Keto-1-phenyl-1:2-dihydroquinoxaline-3-carboxylic acid,

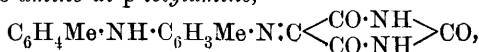


prepared by boiling alloxanylphenyl-*o*-phenylenediamine with an excess of sodium carbonate, separates from dilute alcohol in leaflets and melts at 177°. It forms a reddish-yellow solution with concentrated sulphuric acid, and a yellow solution with hydrochloric or with nitric acid. Its barium salt forms yellow needles.

2-Keto-1-phenyl-1:2-dihydroquinoxaline, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} = \text{CH} \\ \text{NPh} \cdot \text{CO} \end{smallmatrix}$, prepared

by heating the preceding acid above its melting point until the evolution of carbon dioxide ceases, separates from dilute alcohol in bright yellow needles and melts at 167°. Its solution in concentrated sulphuric acid is green, and on dilution becomes red and then yellow; its solution in hydrochloric or nitric acid is yellowish-red.

Alloxanyl-o-amino-di-p-tolylamine,



prepared from alloxan and *o*-amino-di-*p*-tolylamine, separates from glacial acetic acid in yellow needles and melts at 244°. Its solution in sulphuric acid is cherry-red; its solution in hydrochloric or nitric acid is reddish-yellow.

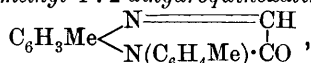
p-Toluidino-*m*-tolyliminoalloxanic acid,

$\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}:\text{C}(\text{CO}_2\text{H})\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, prepared by the action of cold dilute sodium hydroxide on the preceding compound, melts at 240°.

2-Keto-1-p-tolyl-6-methyl-1 : 2-dihydroquinoxaline-3-carboxylic acid,

$\text{C}_6\text{H}_3\text{Me}\begin{matrix} \text{N} \\ \diagup \quad \diagdown \\ \text{C}\cdot\text{CO}_2\text{H} \\ \diagdown \quad \diagup \\ \text{N}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CO} \end{matrix}$, prepared by boiling alloxanyl-*o*-amino-di-*p*-tolylamine with sodium carbonate, separates from dilute alcohol in hexagonal leaflets and melts at 194°. It forms a reddish-yellow solution with concentrated sulphuric acid and a yellow solution with hydrochloric or nitric acid. Its *barium* salt (+ 4½H₂O) and *zinc* salt (+ 2H₂O) are described.

2-Keto-1-p-tolyl-6-methyl-1 : 2-dihydroquinoxaline,



prepared by heating the preceding acid above its melting point, forms yellow needles and melts at 170—171°. Its solution in sulphuric acid is brown, and on dilution becomes red and then yellow.

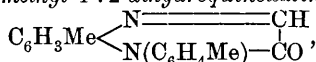
p-Toluidino-*p*-tolyliminoalloxanic acid,

$\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}:\text{C}(\text{CO}_2\text{H})\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, prepared by shaking alloxanyl-*o*-amino-*m*-tolyl-*p*-tolylamine with dilute sodium hydroxide, crystallises in leaflets and partially melts at 180°, solidifies, and melts again at 248°.

2-Keto-1-p-tolyl-7-methyl-1 : 2-dihydroquinoxaline-3-carboxylic acid,

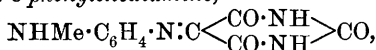
$\text{C}_6\text{H}_3\text{Me}\begin{matrix} \text{N} \\ \diagup \quad \diagdown \\ \text{C}\cdot\text{CO}_2\text{H} \\ \diagdown \quad \diagup \\ \text{N}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CO} \end{matrix}$, crystallises from dilute alcohol in tetragonal leaflets and melts at 193°. Its *barium* salt (+ 1½H₂O) forms yellow needles.

2-Keto-1-p-tolyl-7-methyl-1 : 2-dihydroquinoxaline,



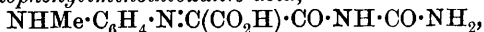
separates from dilute alcohol in yellow needles and melts at 173°. Its solution in sulphuric acid is brown, and becomes red and then yellow on dilution. Its solution in hydrochloric or nitric acid is yellow.

Alloxanylmethyl-o-phenylenediamine,

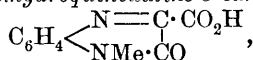


prepared from alloxan and *N*-methyl-*o*-phenylenediamine, separates from glacial acetic acid in yellow needles and melts at 224°. Its solution in sulphuric acid is cherry-red, and in hydrochloric or nitric acid yellowish-red.

The *acetyl* derivative, $\text{NMeAc}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{C}\begin{matrix} \text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 \\ \diagdown \quad \diagup \\ \text{CO}_2\text{H} \end{matrix}$, crystallises in needles and melts and decomposes at 265—270°.

Methylaminophenyliminoalloxanic acid,

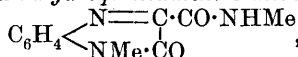
prepared by the action of sodium carbonate on alloxanylmethyl-*o*-phenylenediamine, separates from a mixture of acetone and light petroleum in needles and melts at 224°. Its solutions in concentrated mineral acids are red.

2-Keto-1-methyl-1 : 2-dihydroquinoxaline-3-carboxylic acid,

prepared by boiling alloxanylmethyl-*o*-phenylenediamine with sodium carbonate until the evolution of ammonia ceases, forms yellow needles and melts at 174°. Its solution in sulphuric acid is reddish-yellow, and in hydrochloric or nitric acid yellow. Its *barium* salt (+ 1½H₂O) forms needles.

2-Keto-1-methyl-1 : 2-dihydroquinoxaline, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{N} = \text{CH} \\ \diagdown \text{NMe} \cdot \text{CO} \end{array}$, separates

from dilute acetone in yellowish-white needles and melts at 122°. It forms a yellowish-green solution with sulphuric acid and a yellow solution with hydrochloric or nitric acid.

2-Keto-1-methyl-1 : 2-dihydroquinoxaline-3-methylamide,

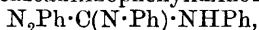
prepared from methyl-*o*-phenylenediamine and methylalloxan, crystallises from dilute alcohol in yellow needles and melts at 166°. Its solution in sulphuric acid is cherry-red. When boiled with potassium or sodium hydroxide, it forms 2-keto-1-methyl-1 : 2-dihydroquinoxaline-3-carboxylic acid.

A. McK.

Tetrazoline. Reply to R. Stollé. SIEGFRIED RUHEMANN (*Ber.*,

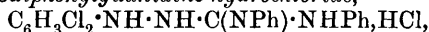
1906, 39, 1228—1231).—Dimethyltetrazoline, $\text{CMe} \begin{array}{c} \diagup \text{N} \cdot \text{NH} \\ \diagdown \text{NH} \cdot \text{N} \end{array} \text{CMe}$, yields with methyl iodide a colourless *iodide*, $\text{C}_5\text{H}_{11}\text{N}_4\text{I}$, from which a brown *periodide*, $\text{C}_5\text{H}_{11}\text{N}_4\text{I}_3$, can be obtained. Alkaline solutions of this periodide do not become violet on exposure to air.

The original formula for benzyldenetetrazoline (Ruhemann and Merriman, *Trans.*, 1905, 87, 1768) is retained, and it is suggested that the products obtained from *s*-diphenyltetrazoline and aldehydes may be differently constituted (compare Stollé, this vol., i, 315). J. J. S.

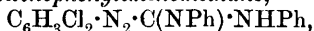
Behaviour of Certain Azo-compounds towards Hydrogen Chloride. MAX BUSCH and HERMANN BRANDT (*Ber.*, 1906, 39, 1395—1400).—Benzeneazoanilinophenyliminomethane,

is dissolved by alcoholic hydrogen chloride to a colourless solution, from which the *hydrochloride* of *p*-chloroanilindiphenylguanidine, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{NH} \cdot \text{C}(\text{NPh}) \cdot \text{NHPh}$, can be obtained. A second, but not a third, halogen atom can be introduced in a similar way into an *ortho*-position in the same nucleus (compare Marckwald and Wolff, *Abstr.*, 1893, i, 25; Hantzsch and Singer, *ibid.*, 1897, i, 216; Jacobsen, *Chem. Centr.*, 1898, ii, 36; Bamberger, *Abstr.*, 1902, i, 246).

p-Chloroanilindiphenylguanidine crystallises in pale red prisms and melts at 154°. The hydrochloride, $C_{19}H_{17}N_4Cl \cdot HCl$, forms clusters of colourless prisms and melts at 216°. The base in boiling alcoholic solution is converted by mercuric oxide into *p*-chlorobenzene-azoanilinophenyliminomethane, $C_6H_4Cl \cdot N_2 \cdot C(NPh) \cdot NPh$, which crystallises in blood-red, glistening needles and melts at 155°. 2:4-Dichloroanilindiphenylguanidine hydrochloride,



obtained from the preceding compound and alcoholic hydrogen chloride at 40–50°, crystallises in obliquely truncated, flattened prisms, darkens at 225°, and melts and decomposes at 242°. The base, $C_{19}H_{16}N_4Cl_2$, crystallises in colourless prisms and melts at 125°. 2:4-Dichlorobenzeneazoanilinophenyliminomethane,



crystallises in small, brownish-red needles and melts at 130°. Cold alcoholic hydrogen chloride dissolves it, forming a reddish-brown solution, from which the hydrochlorides of aniline and of dichloroanilindiphenylguanidine are obtained, but not a trichloro-derivative.

C. S.

Diazotation of Dibenzoylmethane. HEINRICH WIELAND and SIEGFRIED BLOCH (*Ber.*, 1906, 39, 1488–1491. Compare Abstr., 1904, i, 596, 656).—Dibenzoyldiazomethane has the constitution of a diazoanhydride,

$\begin{array}{c} CPh \cdot O \\ || \\ CBz \cdot N \end{array} \gg N$, as when treated with ammonium and hydrogen sulphides in alcoholic solution it yields 4-benzoyl-5-phenyl-

1:2:3-thiodiazole, $\begin{array}{c} CPh \cdot S \\ || \\ CBz \cdot N \end{array} \gg N$, which crystallises in glistening, colourless scales, melts at 90–91°, and becomes violet, and finally yellow on exposure to light.

Anilindibenzoylmethane forms a yellow, crystalline *nitrosoamine*, $CHBz_2 \cdot NPh \cdot NO$, which melts and decomposes at 92° and gives Liebermann's reaction.

G. Y.

Azo-dye from *m*-Aminobenzeneazo-*m*-toluidine. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 162627).—Diazotised *m*-aminobenzeneazo-*m*-toluidine combines with β -naphthol to form an insoluble bordeaux-red azo-dye, which may be bleached white in printing by means of the formaldehyde-hyposulphite compound.

C. H. D

Equilibrium between Proteids and Electrolytes. II. Precipitation of Egg-albumin with Sodium Sulphate. G. GUERRINI (*Zeit. physiol. Chem.*, 1906, 47, 287–293. Compare Galeotti, *ibid.*, 1904, 40, 5).—The precipitation of egg-albumin by means of sodium sulphate depends on the concentration of the sulphate solution, and the solid phase obtained consists of egg-albumin only. This is proved by showing that the precipitate contains only an amount of sulphate corresponding with what should be present in the amount of solution of known concentration absorbed by the precipitate.

A simple method is described for estimating the amounts of water, albumin, and sodium sulphate in a solution.

It is shown that in the three-component system containing the phases $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$ solid, albumin (solid), solution, the concentration of the solution can vary considerably even when the temperature is constant. There appears, however, to be a regularity between the variations in the concentration of the albumin and of the sulphate.

This exception to the phase rule may be due to the fact that one of the substances is a colloid. J. J. S.

Precipitation of Egg-albumin by other Colloids and its Relationship to the Reactions of Immune Substances. ULRICH FRIEDEMANN (*Arch. Hygiene*, 1906, 55, 361—389. Compare Abstr., 1904, ii, 546).—Serum and egg-albumin are precipitated by inorganic colloids, such as metals, sulphides, acid oxides, or basic oxides, irrespective of whether these are electro-positive or electro-negative in character. The influence of the addition of salts is partly accelerating and partly retarding, the net result depending on the relative proportions of colloid and albumin in the mixture. The sign of the electric potential of the albumin compared with water does not control its precipitation by inorganic colloids, inasmuch as Hardy's coagulated egg-albumin, which wanders to the anode, gives copious precipitates with every colloid investigated. The precipitating power of ions is a function of their dielectric attraction on the water. The rôle of salts in precipitin reactions is very similar to that in colloid albumin precipitations, an amphoteric colloid probably reacting with an acid or a basic colloid. Bacteria can be agglutinated by a salt-free serum even in such dilutions as 1 : 1000. In this respect, normal and immune sera behave alike. E. F. A.

Compounds of Catechol Monoalkyl Ethers with Proteids. H. C. FEHRLIN (D.R.-P. 162656).—When guaiacol, either fused or dissolved in alcohol, is stirred into an aqueous solution of egg-albumin, the whole soon solidifies to a paste. The product is collected, drained, dried under reduced pressure, and heated at 115—120°, when it becomes insoluble in gastric juice. After washing with toluene and again drying, it forms a light brown powder, containing 25 per cent. of guaiacol, insoluble in ordinary solvents, but soluble in cold dilute alkali hydroxides.

Similar products are obtained from other monoalkyl ethers of catechol, and from other proteids, albumoses, and peptones: The compounds find therapeutic application. C. H. D.

Polymerisation of Globulins. ALONZO E. TAYLOR (*J. Biol. Chem.*, 1906, 1, 345—354).—Euglobulin and pseudo-globulin prepared from serum, when dry, remain unchanged for years. In presence of distilled water, each is partly transformed into the other. This is a reversible action, and is attributed to polymerisation. As in other instances quoted, there is a tendency to equilibrium in the system, and the law of mass action holds. Viewed as a chemical transformation, three possibilities are discussed: (1) condensation, (2) union with

water, and (3) intramolecular rearrangement. The transformation of albumin into globulin is believed to come into the same category. Further, it was found that the globulins in distilled water, and especially the pseudo-globulins, are in part auto-hydrolysed with the formation of proteoses.

W. D. H.

Hæmatogen and the Formation of Hæmoglobin. LOUIS HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1906, 142, 805—806. Compare Abstr., 1905, ii, 566; 1906, ii, 95).—Hæmatogen, the parent substance of hæmoglobin in egg-yolk, yields a proteid residue, which, like globin and other histones, is rich in diamino-nitrogen. It also yields on hydrolysis a black pigment (C, 65.9; H, 4.37; N, 6.67, and Fe, 2.6 per cent.) which is regarded as analogous to hæmatin, and named *hæmatovin*. It is possible that hæmatovin may be an intermediate stage in hæmatin formation during life. In chlorosis, Seiller and Freund have found in the blood an uncoloured nucleo-proteid containing iron. It is possible the presence of such a substance may account for discrepancies between estimations of iron and of hæmoglobin in the blood.

W. D. H.

Bile Pigments. WILLIAM KÜSTER (*Zeit. physiol. Chem.*, 1906, 47, 294—326).—By working with powdered gall stones, the use of hydrochloric acid can be avoided, and 10 per cent. acetic acid employed instead. Hot glacial acetic acid extracts a hitherto undescribed green pigment, *choleprasin*; it is insoluble in alcohol. β -Bilirubin is easily soluble in chloroform and is an artificial product which contains chlorine; from it the chlorine is easily separable. Most impure bilirubins obtained by chloroform contain chlorine. From pure bilirubin by the action of chloroform in the dark, a green pigment soluble in glacial acetic acid is formed in small quantities. On keeping, bilirubin undergoes a change, probably a polymerisation. This modification passes by recrystallisation from dimethylaniline into the form soluble in chloroform. Bilirubin crystallises from hot dimethylaniline in broad rhombic plates or from chloroform in long needles.

W. D. H.

The Carbohydrate Group of the Nucleo-proteid of the Spleen. I. PHOEBUS A. LEVENE and JOHN A. MANDEL (*Zeit. physiol. Chem.*, 1906, 47, 151—153).—The carbohydrate group in nucleo-proteid is usually a pentose (xylose). The nucleo-proteid of the spleen after suitable treatment gave the orcinol reaction for pentose, and reduced Fehling's solution after preliminary treatment with hydrochloric acid. Glucothionic acid was also separated, but it is not clear whether this came from the nucleo-proteid or from mucoid mixed with it.

W. D. H.

Nucleic Acids. XII. Nucleic Acid of the Kidney. JOHN A. MANDEL and PHOEBUS A. LEVENE (*Zeit. physiol. Chem.*, 1906, 47, 140—142. Compare this vol., i, 125).—The occurrence of nucleo-proteid in the kidney has been described by Halliburton and by Lönnberg, but its products of decomposition have not been investigated.

In the present research, the nucleic acid separated from the nucleoproteid contained 6.25 per cent. of phosphorus, and yielded, on decomposition with acid, guanine, adenine, thymine, cytosine, and lævulic acid. One hundred grams of substance yielded adenine picrate 2.20, guanine 7.32, thymine 3.6, and cytosine picrate 12.24 grams. The nucleic acid gave the typical pentose reaction with orcinol hydrochloride.

W. D. H.

Jecorin. RICHARD WALDVOGEL and TINTEMANN (*Zeit. physiol. Chem.*, 1906, 47, 129—139).—Jecorin obtained from autolysed livers and spleen contains from 8 to 9.8 per cent. of nitrogen and from 2 to 3.4 per cent. of phosphorus. These numbers are very different from those obtained by other observers; for instance, Drechsel gives the percentage of nitrogen as 4.36, Baldi as 2.14, and Manasse as 0.3. The authors, nevertheless, regard it as a chemical individual, derived from lecithin. Some preparations reduced Fehling's solution, some did not.

W. D. H.

Decomposition of Gelatin. PHOEBUS A. LEVENE and GEORGE B. WALLACE (*Zeit. physiol. Chem.*, 1906, 47, 143—148. Compare Abstr., 1903, i, 301; 1904, i, 357).—On tryptic digestion of gelatin, the pyrrolidine-2-carboxylic acid formed is identical with the optically inactive pyrrolidine-2-carboxylic acid. After fifteen months' digestion of 1500 grams of gelatin with trypsin, the mixture was neutralised, evaporated to a syrupy consistency, taken up in 5 per cent. sulphuric acid, and fractionally precipitated with phosphotungstic acid. From the first precipitate, a substance was separated of the formula $C_7H_{10}O_2N_2$; further work on this is in progress. From the fourth precipitate, glycine was separated. The other precipitates are not yet examined.

W. D. H.

Swelling of Gelatin in Salt Solutions. WOLFGANG OSTWALD (*Pflüger's Archiv*, 1906, 111, 581—606. Compare Abstr., 1905, i, 845, 954).—In regard to the influence of salts on the swelling of gelatin, the influence of concentration of acids, alkalis, chlorides, and nitrates was found to be of a specific nature, and the curves show no parallelism to a single factor (such as osmotic pressure), but present several maxima and minima. The first part of such curves indicates adsorption is occurring for reasons which are explained in full. There is further a parallelism between the curve of swelling and that of viscosity.

W. D. H.

Action of the Rennet Ferment on Casein. EUGEN PETRY (*Chem. Centr.*, 1906, i, 1032; from *Wien. Klin. Woch.*, 19, 143—144).—The action of rennet on casein free from calcium does not cease with the formation of paracasein. The nature of the action as regards products is similar to that of ordinary proteolytic ferments. Primary albumoses (caseose) are formed, as well as a modification of paracasein which is not precipitated by lime, by heating, or by dilute zinc sulphate.

Rennet extract (Merck) is without action on serum albumin, boiled egg-albumin, and gelatin.

N. H. J. M.

Influence of Peroxydase on Alcoholic Fermentation. ALEXIS BACH (*Ber.*, 1906, **39**, 1664—1668).—An aqueous solution of sucrose was acted on by a mixture of peroxydase (prepared as in former experiments by the author) and hydrogen peroxide in the presence of the solid precipitated from yeast juice by the addition of acetone ("Aceton-Dauerhefe"). The effect of the peroxydase as estimated by the volume of carbon dioxide produced was thus studied. The whole of the hydrogen peroxide present was decomposed with the evolution of oxygen. The presence of the active peroxydase has a strong inhibiting action on alcoholic fermentation in the cases studied. When the peroxydase is first boiled and then added to the solution containing sucrose, &c., the presence of the hydrogen peroxide has no inhibiting effect; hydrogen peroxide in the absence of peroxydase also has no inhibiting effect. The presence of peroxydase and of hydrogen peroxide has no effect on the acidity of the liquid after fermentation.

The capability which the solid precipitated from yeast juice by acetone possesses of liberating oxygen from hydrogen peroxide is diminished by the presence of active peroxydase. A. McK.

Fate of Yeast Catalase in Cell-free Alcoholic Fermentation. ALEXIS BACH (*Ber.*, 1906, **39**, 1669—1670. Compare preceding abstract).—The author has examined the diminution in the amount of catalase of precipitated yeast juice during alcoholic fermentation and draws the conclusions: (1) that the amount of catalase in precipitated yeast juice decreases regularly, although slowly, during autolysis, (2) that, in the presence of sucrose, the destruction of the catalase is very much quicker than during autolysis, and (3) that the destruction of the catalase increases in both cases with diminution of the concentration of the precipitated yeast juice. A. McK.

Influence of Peroxydase on the Activity of Catalase. ALEXIS BACH (*Ber.*, 1906, **39**, 1670—1672. Compare preceding abstracts).—Yeast catalase did not diminish in activity on prolonged contact with active peroxydase at 30°. A. McK.

Alcoholic Ferment of Yeast Juice. ARTHUR HARDEN and WILLIAM J. YOUNG (*Proc. Roy. Soc.*, 1906, **77**, B, 405—420. Compare *Proc.*, 1905, **21**, 189; *Abstr.*, 1905, ii, 109; also Buchner and Antoni, this vol., i, 56).—The total fermentation produced by yeast juice acting on excess of dextrose is, as a rule, doubled by the addition of an equal volume of boiled and filtered juice, and further increased by a greater volume, the sugar concentration being kept constant. The constituent of the juice to which this effect is due is removed when the liquid is dialysed in a parchment tube, leaving an inactive residue. It is possible by filtering the juice through a Martin gelatin filter to divide the yeast-juice into an inactive residue and a dialysate which, although itself inert, is capable of rendering this residue active.

Two phenomena are concerned in the production of the increased fermentation in the presence of boiled yeast juice: (a) an initial rapid evolution of carbon dioxide is produced which soon diminishes

until a rate is attained which remains nearly constant for several hours; (b) the fermentation rate diminishes more slowly, so that fermentation continues for a longer period. To the latter the greater proportion of the total increase is due.

The extra quantity of carbon dioxide evolved in the initial period is directly proportional to the volume of boiled juice added. A similar initial rapid evolution of gas is produced on the addition of soluble phosphates, the increase corresponding exactly with the amount of phosphate added. A second rapid evolution of carbon dioxide sets in on adding a second quantity of phosphate after a steady rate is attained subsequent to the first addition. Fermentation in the presence of phosphates is a normal alcoholic fermentation, the ratio of alcohol to carbon dioxide being 1.13. The soluble phosphate is converted into a non-precipitable form by the reaction, possibly into a phosphoric ester of dextrose.

E. F. A.

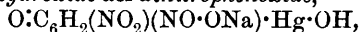
Mercurinitrophenols. ARTHUR HANTZSCH and SAMUEL M. AULD (*Ber.*, 1906, 39, 1105—1117).—Two types of nitrophenol derivatives containing mercury have been obtained, the true mercuric nitrophenoxides exhibiting in solution the reactions of mercury ions, and mercurinitrophenols in which the atom of mercury is attached to the benzene nucleus. The latter compounds usually resemble the nitrophenols in chemical behaviour and absorption of light, and are therefore regarded as solid solutions of the *aci*-form in the true colourless mercurinitrophenols, $\text{HO} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NO}_2 \\ \text{HgX} \end{smallmatrix} \rightleftharpoons \text{O} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NO} \cdot \text{OH} \\ \text{HgX} \end{smallmatrix}$. From the mercuric nitrophenoxides, intensely-coloured anhydrides are obtained to which formulæ such as $\text{O} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NO} \\ \text{Hg} \end{smallmatrix} \text{O}$ are ascribed.

Mercuripicric anhydride, $\text{O} \cdot \text{C}_6\text{H}(\text{NO}_2)_2 \begin{smallmatrix} \text{NO} \\ \text{Hg} \end{smallmatrix} \text{O}$, is obtained by boiling for several hours freshly-precipitated mercuric oxide with an aqueous solution of picric acid. It forms small, pale yellow crystals, decomposes without melting, is a non-electrolyte in aqueous solution, and does not show the reactions of mercuric ions. Dilute hydrochloric acid converts it into *mercurichloride-trinitrophenol*, $\text{OH} \cdot \text{C}_6\text{H}(\text{NO}_2)_3 \cdot \text{HgCl}$, which separates from chloroform in small crystals with a faint yellow colour and melts at 118°. When treated with sodium hydroxide, it yields *sodium mercurihydroxide-picrate*, $\text{O} \cdot \text{C}_6\text{H}(\text{NO}_2)_2(\text{NO} \cdot \text{ONa}) \cdot \text{Hg} \cdot \text{OH}$, which separates from alcohol in yellow needles and decomposes by rapid heating. *Mercurihydroxide-picric acid*, $\text{OH} \cdot \text{C}_6\text{H}(\text{NO}_2)_3 \cdot \text{Hg} \cdot \text{OH}$, results by the action of dilute sulphuric acid on the preceding compound or directly on the anhydride, and is obtained colourless from alcohol or acetone.

Mercuri-aci-2:4-dinitrophenol anhydride, $\text{O} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \begin{smallmatrix} \text{NO} \\ \text{Hg} \end{smallmatrix} \text{O}$, is obtained by boiling freshly-precipitated mercuric oxide for sixteen hours with an aqueous solution of the calculated quantity of dinitrophenol. It is obtained pure as a pale yellow powder by heating its compound with pyridine, $\text{C}_6\text{H}_5\text{O}_5\text{N}_2\text{Hg} \cdot \text{C}_5\text{NH}_5$, and in aqueous solution does not yield mercury ions. The replacement of mercury by bromine leads to

the formation of *o*-bromodinitrophenol. *Mercurichloride-dinitrophenol*, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{HgCl}$, obtained from the anhydride and dilute hydrochloric acid, is a colourless crystalline powder and melts and blackens at 182° ; by the Schotten-Baumann reaction, a colourless benzoyl derivative is obtained.

Sodium mercurihydroxide-aci-dinitrophenoxide,



obtained from the chloride by the action of concentrated sodium hydroxide, separates from water or dilute alcohol in orange-red prisms containing $1\text{H}_2\text{O}$ and explodes when strongly heated. Dilute sulphuric acid converts it into *mercurihydroxide-dinitrophenol*,



which separates from alcohol as a colourless, microcrystalline powder.

Mercuri-aci-p-nitrophenol anhydride, $\text{O}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{NO} \\ \text{Hg} \end{smallmatrix} \text{O}$, is a yellow powder obtained by the prolonged boiling of a dilute alcoholic solution of mercuric acetate and sodium *p*-nitrophenoxide. The pyridine compound, $\text{C}_6\text{H}_3\text{O}_3\text{NHg}\cdot\text{C}_5\text{NH}_5$, is a scarlet powder and decomposes at 190° into its constituents. The mercury must be ortho to the hydroxyl group, since 2:6-dibromo-*p*-nitrophenol does not yield a corresponding derivative.

Mercurichloride-p-nitrophenol, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{HgCl}$, is colourless and melts at 175° . *Sodium mercurihydroxide-aci-p-nitrophenoxide*, $\text{O}\cdot\text{C}_6\text{H}_3(\text{NO}\cdot\text{ONa})\cdot\text{Hg}\cdot\text{OH}$, crystallises with $\frac{1}{2}\text{H}_2\text{O}$ and darkens and decomposes on heating.

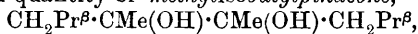
Mercurihydroxide-p-nitrophenol separates from boiling alcohol as an amorphous powder and melts at 206° ; its solutions in acetone, alcohol, or acetic acid are colourless, in pyridine faintly yellow.

Mercuri-aci-o-nitrophenol anhydride, $\text{O}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{Hg} \\ \text{NO} \end{smallmatrix} \text{O}$, is a yellow powder and by treatment with bromine yields *p*-bromo-*o*-nitrophenol. *Mercurichloride-o-nitrophenol*, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{HgCl}$, forms colourless solutions in acetic acid or acetone, but dissolves in pyridine with a yellow colour. *Sodium mercurihydroxide-o-nitrophenoxide* separates from dilute alcohol in dark red crystals. *Mercurihydroxide-o-nitrophenol* forms pale yellow crystals and melts and decomposes at $240\text{--}250^\circ$.

C. S.

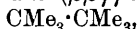
Organic Chemistry.

isoHexane and a New Dodecane. LATHAM CLARKE and R. NORRIS SHREVE (*Amer. Chem. J.*, 1906, **35**, 513—519).—*iso*-Hexane (ethylisobutyl) can be prepared in a yield of 57 per cent. of the theoretical by the reduction of methylisobutylcarbinol. Methylisobutyl ketone, prepared by boiling ethyl isopropylacetoacetate for six hours with 10 per cent. potassium hydroxide, boils at 119° under 765 mm. pressure. Methylisobutylcarbinol can be obtained by mixing an ethereal solution of the ketone with water and gradually adding sodium; a small quantity of methylisobutylpinacone,



is produced simultaneously as a viscous, oily liquid which has a fishy odour, boils at 245°, and is soluble in alcohol, ether, ethyl acetate, acetone, benzene, or glacial acetic acid, and insoluble in water. On reducing this pinacone with hydrogen iodide, methylisobutylcarbinyl iodide, $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CHMeI}$, is obtained as a colourless, oily liquid which boils and partially decomposes at 158—160°, and is soluble in the usual organic solvents, but insoluble in water. The formation of this iodide is attended by the production of a small quantity of a dodecane (dimethyldiisobutylethane), $\text{CH}_2\text{Pr}^\beta \cdot \text{CHMe} \cdot \text{CHMe} \cdot \text{CH}_2\text{Pr}^\beta$, which forms a colourless, oily liquid with a faint odour, boils at 208—210°, and is soluble in light petroleum, and slightly so in alcohol. E. G.

Hexamethylethane. LOUIS HENRY (*Compt. rend.*, 1906, **142**, 1075—1076).—Hexamethylethane ($\beta\beta\gamma\gamma$ -tetramethylbutane),



is an accessory product in the synthesis of pinacolyl alcohol by the interaction of acetaldehyde and magnesium *tert*-butyl bromide. It crystallises from ether in barbed lamellæ, has a piquant, penetrating odour, melts at 103—104°, and boils at 106—107° under 765 mm. pressure.

T. A. H.

Composition of Light Petroleum. LUIGI BALBIANO and VINCENZO PAOLINI (*Gazzetta*, 1906, **36**, i, 251—256. Compare Abstr., 1902, ii, 109).—Fourteen kilos. of American petroleum gave 3.5 grams of mercurous acetate when treated with mercuric acetate, whilst acetone and propaldehyde were found in the solution. These may have been formed by oxidation of β -methyl- Δ^2 -pentylene.

T. H. P.

New Constituents of Coal Tar. FELIX B. AHRENS (*Chem. Centr.*, 1906, i, 510—511; from *Verh. Ges. Deut. Naturforsch. Aerzte*, 1904, ii, 137—138. Compare Abstr., 1903, i, 515; 1904, i, 615; 1905, i, 232).—In a fraction from the benzene receiver which boiled at 20—30°, butylene and a compound which contained sulphur and resembled carbon disulphide, but was not identical with it, have

been found. Amylene was isolated from a fraction boiling at 30—40°. 2:3-Dimethylpyridine has been obtained from a commercial sample of $\alpha\beta$ -picoline; it boiled at 162—163° and yielded a picrate which melted at 183° and was almost insoluble in alcohol or water.

E. W. W.

Decomposition of Bromoform under the Influence of Light and Air. NICOLAAS SCHOORL and L. M. VAN DEN BERG (*Chem. Centr.*, 1906, i, 441—442; from *Pharm. Weekblad*, 43, 2—8. Compare this vol., i, 57).—When a current of air is passed through boiling bromoform in sunlight, bromine, hydrogen bromide, and carbon tetrabromide are produced. The primary reactions have already been investigated in the case of chloroform and iodoform. By the action of light in the presence of oxygen, carbon monoxide is oxidised to the dioxide, hydrogen bromide forms water and bromine, and by the action of the latter on bromoform, carbon tetrabromide and hydrogen bromine are obtained.

When bromoform, together with a small quantity of oxygen, is exposed to sunlight in sealed tubes, the action appears to result in the formation of carbon monoxide (1 mol.), bromine (1 mol.), and hydrogen bromide (1 mol.); when a large quantity of oxygen is present, carbon dioxide (2 mols.), water (1 mol.), and bromine (3 mols.) are formed. Carbon oxybromide is an intermediate product. When bromoform is exposed to sunlight in tubes from which the air has been almost completely removed, carbon monoxide and hydrogen bromide are obtained in the proportion of 13.7 to 47 1/10-equivalents; this result is consistent with the hypothesis that the bromoform is decomposed into carbon dibromide and hydrogen bromide, and that the former is decomposed by the water in the wash-bottles, forming carbon monoxide and hydrogen bromide. In addition to these products, 12 1/10-equivalents of bromine are also liberated. The liberation of bromine must be assumed to result from the intermediate formation of some other carbon hydrogen bromine compound, possibly of symmetrical tetrabromoethane, $\text{CHBr}_2\text{CHBr}_2$, and the decrease of sp. gr. of the contents of the tube from 2.882 to 2.872 at 19° may be an indication of this change. The presence of carbon tetrabromide could not be detected in this case.

E. W. W.

Comparison of the Decomposition of Chloroform, Bromoform, and Iodoform under the Influence of Light NICOLAAS SCHOORL and L. M. VAN DEN BERG (*Chem. Centr.*, 1906, i, 442; from *Pharm. Weekblad*, 43, 8—10. Compare preceding abstract).—Experiments on the action of light alone on chloroform, bromoform, and iodoform have shown that whilst chloroform is not affected, iodoform is partially decomposed in consequence of the presence of traces of air, and bromoform is decomposed spontaneously, probably forming carbon dibromide and hydrogen bromide. By the action of air in the absence of sunlight at higher temperatures, iodoform becomes violet in a quarter of an hour, and the separation of iodine is distinctly visible in an hour; bromoform becomes acid and slightly yellow

in an hour, and gives a precipitate with silver nitrate, whilst chloroform does not give any reaction with silver nitrate after four hours.

E. W. W.

Decomposition of Iodoform dissolved in Chloroform by Diffused Daylight and by Radium Rays. WILLEM P. JORISSEN and WILHELM E. RINGER (*Chem. Centr.*, 1906, i, 442; from *Chem. Weekblad*, 2, 799—802. Compare preceding abstracts).—When a solution of iodoform in chloroform is exposed to diffused sunlight in the presence of oxygen, it appears to be completely decomposed. A solution of iodoform in carbon disulphide covered with water does not show any change for some time, and then decomposes only very slowly. A solution of iodoform in chloroform frozen by means of liquid air is not affected by bright daylight so long as it remains solid.

By the action of 5 mg. of radium bromide on 50 c.c. of a 1 per cent. solution of iodoform in chloroform at 25°, 75·2 per cent. of the iodine was liberated, whilst in a similar solution which was not exposed to the action of radium bromide only 18·8 per cent. of the iodine was found in a free state. The colour of the iodine solution formed by the action of the radium bromide was not so dark as that of similar solutions obtained by the action of daylight.

E. W. W.

Abnormality in Melting Points of Amides derived from Aliphatic Sulphonic Acids. MAURICE DUGUET (*Bull. Acad. roy. Belg.*, 1906, 87—120).—*isoPropanesulphonic chloride*, $\text{CHMe}_2\cdot\text{SO}_2\text{Cl}$, prepared from phosphorus pentachloride and the corresponding alkali sulphonate, boils at 79° under 18 mm. pressure. Its solution in ether on treatment with dry ammonia yields the corresponding *sulphonamide*, which crystallises from ether on addition of light petroleum and melts at 60°. *isoPropanesulphonanilide* crystallises from a mixture of alcohol and water in colourless, pearly leaflets and melts at 84°. *isoPropanesulphon- α -naphthylamide* crystallises from a mixture of alcohol and water in slender needles and melts at 134°. *Butanesulphonic chloride* is a mobile, highly-refractive liquid, and boils at 96—97° under 18 mm. pressure. *Butanesulphonamide* crystallises from a mixture of ether and light petroleum in silky leaflets and melts at 45°. The corresponding *anilide* melts between -10° and -15° and the *α -naphthylamide* in colourless spangles melting at 60·5°.

Methanesulphon- α -naphthylamide crystallises in slender, silky needles and melts at 125—126°. *Ethanesulphon- α -naphthylamide* forms long, colourless prisms and melts at 66°. *Propanesulphon- α -naphthylamide* melts at 84°. *isoButanesulphon- α -naphthylamide* crystallises in colourless spangles and melts at 107°. *isoPentanesulphon- α -naphthylamide* forms colourless, pearly spangles and melts at 90—91°.

The melting points of the series of amides, anilides, and α -naphthylamides described in this and the former paper (*Abstr.*, 1902, i, 428) decrease irregularly as each series is ascended; further, whilst the melting-point curve of the amides of the *iso*-acids is below that of the amides of the normal acids, the reverse is true of the curves for the anilides and α -naphthylamides of the *iso*- and normal acids. Similar examples of the fall in melting point as the series are ascended are shown

by the aromatic sulphonamides (Abstr., 1900, i, 147) and the halogen and other derivatives of these described by Chattaway (Trans., 1905, 87, 145). Determinations of the molecular weights of the lower members of the series of compounds now described indicate that in dilute solutions they are not polymerised, but it is not certain that their high melting points are not the result of polymerisation in the solid state. It is pointed out also that there is a possibility of tautomerism in these compounds between the forms $R \cdot SO_2 \cdot NH_2$ and $R \cdot SO(OH) \cdot NH_2$, and that eventually each may be found to exist in two forms having different melting points. Thus, in the case of *isopropane-sulphonamide*, one specimen prepared from *isopropanesulphonic chloride*, which had been kept for seven years, melted at $19-20^\circ$ instead of 60° , but so far it has proved impossible to repeat this experience in the case of this or any other sulphonamide.

T. A. H.

Influence of Oxidation of Ethyl Alcohol on the Maturing of Brandy and Wine. AUGUSTE TRILLAT (*Chem. Centr.*, 1906, i, 580—581; from *Bull. Assoc. Chim. Sucr. Dist.*, 1905, 23, 495—503).—In confirmation of the results obtained by previous workers, it is shown that ethyl, propyl, butyl, and amyl alcohols are readily oxidised spontaneously to acetals, especially in the presence of ferric chloride or hydrochloric acid. Having found that acetals give a blue or green coloration with dimethylaniline and dilute sulphuric acid, owing probably to the formation of compounds of the type $NMe_2 \cdot C_6H_4 \cdot Me \cdot CH \cdot C_6H_4 \cdot NMe_2$, the author has employed the reaction in detecting acetals in a number of brandies and liqueurs, and suggests that the maturing of spirits and wines is due partly to the formation of these acetals, which are highly aromatic substances, and partly to the formation of esters. It has been shown that *Mycoderma vini* materially increases the amount of aldehyde in wine, with the result that the wine becomes turbid, loses its colour, and in the presence of potassium salts may even acquire a bitter taste.

P. H.

Constitution of Pinacolin and its Derivatives. MAURICE DELACRE (*Bull. Acad. roy. Belg.*, 1906, 7—41. Compare Abstr., 1896, i, 591, 662; 1902, i, 79).—The solid chloride, $CMe_3 \cdot CMeCl_2$, obtained by the action of phosphorus pentachloride on pinacolin, is now shown to be identical with Faworsky's chloride, since both on treatment with alcoholic potash furnish the same unsaturated liquid chloride, $CMe_3 \cdot CCl : CH_2$. The existence of an isomeride (boiling point 93°) of this unsaturated chloride, obtained by the action of alcoholic potash on the by-products of the action of phosphoric chloride on pinacolin, is confirmed. By the action of sodium on the liquid chloride, $CMe_3 \cdot CCl : CH_2$, γ -dimethyl- Δ^2 -butylene is produced together with small quantities of an acetylenic hydrocarbon and a paraffin.

Primary pinacolyl acetate, $CMe_3 \cdot CH_2 \cdot CH_2 \cdot OAc$, produced by the action of potassium acetate on the crude γ -dimethyl- Δ^2 -butylene hydrobromide, obtained by the addition of hydrogen bromide to the impure hydrocarbon referred to above, is a colourless liquid, possessing an agreeable fruity odour and boiling at $153-157^\circ$. When hydrolysed with potassium hydroxide, it furnishes primary *pinacolyl alcohol*,

$\text{CMe}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, which is colourless and mobile, has a faint aromatic odour, and solidifies between -60° and -65° . When treated with hydrogen bromide, the alcohol yields the corresponding *pinacolyl bromide*, and this is converted into pinacolyl acetate by potassium acetate, no isomerisation into the symmetrical isomeride taking place. Similarly, no isomerisation into a symmetrical isomeride is brought about by heating the bromide at 100° with hydrobromic acid or by treatment with alkalis. On oxidation with chromic acid, the alcohol yields a mixture of a new *hexoic acid* [$\beta\beta$ -dimethylbutyric acid], $\text{CMe}_3\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (a colourless liquid boiling at 185 — 190°), and the corresponding $\beta\beta$ -dimethylbutaldehyde, $\text{CMe}_3\cdot\text{CH}_2\cdot\text{CHO}$, which boils at 100 — 112° .

The products described in the preceding paragraph are derived in the first instance from the hydrobromide prepared from the crude γ -dimethyl- Δ^a -butylene. If, however, this hydrocarbon in a pure state is treated with hydrogen bromide, it furnishes an additive product, which on treatment with potassium acetate yields no primary pinacolyl acetate, but only $\beta\gamma$ -dimethyl- Δ^b -butylene, $\text{Me}_2\text{C}:\text{CMe}_2$, so that under these circumstances symmetrical isomerisation does occur. These results are in harmony with the abnormal cases recorded by Ipatieff and Dechanoff (Abstr., 1904, i, 705), and it may be assumed that the impurities associated with the crude hydrocarbon in this case exert the same action as the acetic acid employed as a solvent by Ipatieff and Dechanoff.

When the Grignard reaction is applied to isopropyl bromide and acetone, the principal product is probably $\text{CHMe}_2\cdot\text{CMe}_3\cdot\text{OH}$; this, like pinacolyl alcohol, boils at about 120° , and the corresponding bromide on treatment with alcoholic potash yields $\beta\gamma$ -dimethyl- Δ^b -butylene.

When aldehyde is treated with magnesium *tert*.-butyl bromide crotonaldehyde, a crystalline *substance*, which boils at about 110° , and a *hexyl alcohol*, which may have the constitution $\text{CMe}_3\cdot\text{CHMe}\cdot\text{OH}$, are produced. The hexyl alcohol boils at 116 — 125° ; the corresponding *hexyl bromide* boils at 115 — 125° , and when treated with potassium acetate yields $\beta\gamma$ -dimethyl- Δ^b -butylene.

The author discusses the "ketone" and "oxide" formulæ assigned to pinacolin in the light of these new results, and points out that neither is capable of giving a full explanation of the reactions of pinacolin and its derivatives, and that probably no single formula is capable of doing this.

T. A. H.

Synthesis of Pentamethylethanol. LOUIS HENRY (*Compt. rend.*, 1906, 142, 1023—1024).—When ethyl chloroisobutyrate is treated with magnesium methyl bromide dissolved in ether, the pentamethylethanol, $\text{CMe}_3\cdot\text{CMe}_2\cdot\text{OH}$, of Butleroff (Abstr., 1875, 1248) is obtained. The chloride melts at 130° .

T. A. H.

Mode of Formation of Polyhydric Alcohols. WILLIAM OECHSNER DE CONINCK (*Chem. Centr.*, 1906, i, 130; from *Rev. gén. Chim.*, 1905, 8, 347).—The fermentation process by which glycerol is supposed to be formed in plant cells, namely, the reduction of formaldehyde according to the equation $3\text{CH}_2\text{O} + \text{H}_2 = \text{C}_3\text{H}_5(\text{OH})_3$, may in

a similar way give rise to other alcohols. If two atoms of hydrogen react with one, two, three, four, or five molecules of formaldehyde, methyl alcohol, glycol, glycerol, erythritol, or arabitol is formed. Higher members of the series may also be produced in the same manner.

H. M. D.

Vegetable Lecithins. ERNST WINTERSTEIN and O. HIESTAND (*Zeit. physiol. Chem.*, 1906, **47**, 490—498. Compare Abstr., 1904, ii, 141).—The vegetable lecithins vary in their percentage of phosphorus. They yield on hydrolysis, in addition to choline, fatty acids, and glycerophosphoric acid, a considerable amount of sugar, in some cases as much as 16 per cent. The sugar is a mixture of hexoses and pentoses. It is thus doubtful if the vegetable lecithins are the same as those of animal origin. Whether there is any kephalin also is doubtful. It therefore appears wise to adopt the more general term phosphatides for these substances.

W. D. H.

Diffuorochloroacetic Acid. FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1906, 42—51).—*Diffuorochloroacetic acid*, $\text{CClF}_2\cdot\text{CO}_2\text{H}$, is prepared by exposing difluoroacetic acid (Abstr., 1903, i, 727) to the action of dry chlorine in sunlight. The action proceeds slowly, 12 grams of the acid being chlorinated in the course of a month. It fumes on exposure to air, has a strong odour, melts at 22.9° , and boils at 121.5° . In aqueous solution, the maximum electrical conductivity was found to be 392.3 and the coefficient of ionisation 99.66 at a dilution $N/256$. Comparison of these constants with those of trichloroacetic and fluorodichloroacetic acids shows that the substitution of chlorine by fluorine intensifies the acid character. The *potassium*, *barium*, and *silver* salts were prepared. The last-mentioned salt is very unstable, and is slowly hydrolysed by water, forming oxalic, hydrochloric, and hydrofluoric acids. The same decomposition of the silver salt takes place more slowly in alcohol, some ethyl difluorochloroacetate being also formed in this case. A similar hydrolysis of the alkali and alkaline-earth salts occurs in presence of excess of sodium hydroxide. This hydrolysis differs in character from that which takes place with other trihaloid acetic acids under similar conditions, these furnishing usually formic acid and a trihaloid methane. The author has observed a similar difference in the behaviour of the group $\cdot\text{CCl}_2\text{F}$ in toluene derivatives (compare Abstr., 1899, i, 197, and 1900, i, 637).

T. A. H.

Indian Ghedda-wax GEORG BUCHNER (*Chem. Zeit.*, 1906, **30**, 528—529).—In order to show that Ghedda-wax, obtained from the following species of Indian bees, *Apis indica*, *A. dorsata*, or *A. florea*, is in reality closely related to the ordinary beeswax of *Apis mellifica*, the author has determined the melting point, acid saponification, and iodine numbers of specimens of these various waxes, and the results obtained show that qualitatively they are all the same, any differences in composition being due only to the quantitative distribution of the various constituents.

P. H.

Stereoisomerism in the Group of Unsaturated $\alpha\beta$ -Acyclic Acids. EDMOND E. BLAISE and P. BAGARD (*Compt. rend.*, 1906, 142, 1087—1089).—It has been shown previously (*Abstr.*, 1904, i, 369) that the distillation of α -hydroxy-acids in which the hydroxyl group is attached to a secondary carbon atom may be utilised for the preparation of aldehydes. This investigation has now been extended to α -hydroxy-acids in which the hydroxyl group is attached to a tertiary carbon, and it is found that the amount of ketone produced in this distillation decreases as the molecular weight of the acid increases; thus it varies from 48 per cent. in the case of α -hydroxy- α -methylpropionic acid to 5 per cent. in the case of α -hydroxy- α -ethylbutyric acid, and, conversely, the quantity of unsaturated acid simultaneously produced increases. The two acids here mentioned yield lactides, but the production of lactides ceases beyond the C_6 acids of the series.

When the unsaturated acid produced by distillation is capable of existing in two stereoisomeric forms, it is, as a rule, the less stable which preponderates, and this tendency grows as the series is ascended; thus, α -hydroxy- α -methylpropionic acid furnishes angelic and tiglic acids in about equal proportions, but α -hydroxy- α -ethylbutyric acid yields the less stable isomeride almost pure. In cases where a long chain is attached to the alcoholic carbon atom, there may be a migration of the ethylenic linking with the production of some $\beta\gamma$ -unsaturated acid; this occurs in the distillation of α -hydroxy- α -propylvaleric acid. The unsaturated acids obtained by this reaction have been isolated and characterised by conversion into their amides by the method used by Bodroux (*Abstr.*, 1904, i, 662).

The difference between the boiling points of two stereoisomeric unsaturated acids or of their esters decreases as the molecular weight increases. The relative stability towards reagents and heat of the less stable isomerides increases with the molecular weight; thus, whilst tiglic and angelic acids furnish the same bromide, the two ethylcrotonic acids yield different bromides. The less stable isomerides are very sensitive to the action of halogen acids, which transform them into the stable isomerides. Similarly, phosphorus trichloride transforms the less stable isomerides quantitatively into chlorides of the stable acids.

It is pointed out that *cis* and *trans* are no longer suitable descriptive prefixes for the two forms of unsaturated stereoisomeric acids, and it is suggested that they be replaced by the terms *labile* and *stable*, which are abbreviated by the author into *lab.* and *st.* T. A. H.

Ketone-cyanohydrins. A. J. ULTÉE (*Ber.*, 1906, 39, 1856—1858).—In reference to Bucherer and Grolée's work on this subject (this vol., i, 405), the author calls attention to prior work of his own (this vol., i, 5). C. S.

Equilibrium in the System, Glucinum Oxide, Oxalic Anhydride, and Water. CHARLES L. PARSONS and WM. O. ROBINSON (*J. Amer. Chem. Soc.*, 1906, 28, 555—569).—Experiments are described which show that the only definite hydrated oxalates

of glucinum are $\text{GlC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ and $\text{GlC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. The oxalate, $\text{GlC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ (Rosenheim and Woge, Abstr., 1898, ii, 71), forms orthorhombic crystals [$a:b:c=0.853:1.0:1.645$], and is soluble in less than its own weight of water at 100° , and but little less so at the ordinary temperature. The oxalate, $\text{GlC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, is obtained by heating the trihydrate at $100\text{--}105^\circ$.

The acid oxalate described by Rosenheim and Woge (*loc. cit.*) could not be obtained, and the existence of any such salt is considered improbable.

The anhydrous oxalate cannot be obtained, since it is impossible to remove the last trace of water without simultaneously decomposing the oxalate.

An investigation of the so-called basic oxalates of glucinum has shown that these substances are not definite compounds, but consist of solid solutions of the oxalate in the hydroxide. E. G.

Reaction of Nitrous Anhydride with Ethyl Malonate. RICHARD S. CURTISS (*Amer. Chem. J.*, 1906, 35, 477—486. Compare Abstr., 1905, i, 507).—When the gases evolved by the action of warm nitric acid on arsenious oxide are passed into ethyl malonate at 0° , a green oil is formed which consists chiefly of ethyl mesoxalate, together with small quantities of ethyl isonitrosomalonate and of oxalic and acetic acids and their esters. By suitable treatment, the green oil can be made to yield either ethyl oxomalonate, mesoxalic acid, or ethyl mesoxalate.

Ethyl mesoxalate can be thus obtained in a yield of 90 per cent. or more. It is volatile in the air, and distils under $40\text{--}50$ mm. pressure without undergoing any marked decomposition, except the loss of water with formation of ethyl oxomalonate. One gram of water at 22° dissolves 1.3 grams; 1 gram of ethyl malonate dissolves 0.6 gram; and 1 c.c. of benzene at 22° dissolves 0.2 gram of the ester. The ester is also easily soluble in ether, acetone, chloroform, or alcohol.

If ethyl malonate is only partially saturated with the nitrogen oxides, ethyl isonitrosomalonate is obtained; its potassium, silver, sodium, and ammonium salts are described. The observation of Baeyer (*Annalen*, 1864, 131, 293) and of Conrad and Bischoff (Abstr., 1880, 629), that hydrogen cyanide is formed by the decomposition of isonitrosomalonic acid in aqueous solution, could not be confirmed.

If pure crystalline ethyl mesoxalate is heated in a test-tube at its melting point (57°), water condenses on the cool part of the tube, and ethyl oxomalonate remains as a green oil. On cooling the tube and allowing the water to come into contact with the green oil, combination takes place immediately, the green colour disappears, and on touching the colourless liquid with a glass rod, the original crystalline substance is obtained.

Phenylhydrazine reacts with ethyl oxomalonate with formation of an amber-coloured oil which has acid properties and yields a yellow potassium salt. E. G.

Preparation of the Salts of Formaldehydesulphoxylic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 165807).—The salts of

formaldehydesulphoxylic acid are obtained when the formaldehyde-bisulphite compounds or the product of the interaction of formaldehyde and a hyposulphite is treated with reducing agents. Dry sodium hyposulphite is dissolved in 40 per cent. aqueous formaldehyde and the solution heated to boiling for ten minutes with zinc dust and acetic acid. The zinc is then precipitated with sodium carbonate and the filtrate evaporated down under diminished pressure until a solid mass is obtained consisting of sodium formaldehydesulphoxylate mixed with a small proportion of sodium acetate. A similar result is produced by reducing the formaldehydebisulphite compound either with acetic acid and iron filings or aluminium powder, or with stannous chloride.

G. T. M.

Basic Properties of Oxygen. Additive Compounds of the Halogen Acids and Organic Substances containing Oxygen. DOUGLAS MCINTOSH (*J. Amer. Chem. Soc.*, 1906, **28**, 588—590. Compare *Trans.*, 1904, **85**, 919, 1098; 1905, **87**, 784; *Abstr.*, 1905, i, 254, 677).—By the action of the halogen hydrides on acetaldehyde, acetic acid, and ethyl acetate at low temperatures, considerable heat is developed, and the following additive compounds are obtained, which are crystalline, melt sharply, and form supersaturated solutions in the liquid halogen hydride used in their preparation.

The compound $2\text{CH}_3\cdot\text{CHO}, 3\text{HCl}$ melts at -18° , the compound $2\text{CH}_3\cdot\text{CO}_2\text{H}, 3\text{HCl}$ at -53° , and the compound $\text{CH}_3\cdot\text{CO}_2\text{Et}, 2\text{HCl}$ at -75° . The methyl alcohol compound, $3\text{CH}_3\cdot\text{OH}, 2\text{HCl}$, melts at -64° .

The compound $2\text{CH}_3\cdot\text{CHO}, 3\text{HBr}$ melts at -15° , and the compound $2\text{CH}_3\cdot\text{CO}_2\text{Et}, 3\text{HBr}$ at -40° . Acetic acid does not unite with hydrogen bromide or iodide at low temperatures.

The compound $3\text{CH}_3\cdot\text{CHO}, 2\text{HI}$ melts at -32° , and the compound $\text{CH}_3\cdot\text{CO}_2\text{Et}, \text{HI}$ at -23° .

E. G.

Decomposition of Chloral Hydrate by Exposure to Light and Air. NICOLAAS SCHOORL and L. M. VAN DEN BERG (*Chem. Centr.*, 1906, i, 650; from *Pharm. Weekblad*, 1906, **43**, 42—47).—Chloral hydrate, when exposed to tropical sunlight in an exhausted tube, is decomposed according to the following equation: $\text{CCl}_3\text{CHO}, \text{H}_2\text{O} = 3\text{HCl} + 2\text{CO}$. When sealed up in tubes containing an insufficient supply of oxygen, a portion of the substance is also decomposed as follows: $\text{CCl}_3\text{CHO}, \text{H}_2\text{O} + 2\text{O} = 3\text{HCl} + 2\text{CO}_2$, although it may be that the carbon dioxide is only formed by the subsequent oxidation of the monoxide produced according to the first equation. In the presence of an excess of oxygen, the following decompositions take place: $\text{CCl}_3\text{CHO}, \text{H}_2\text{O} + 2\text{O} = 3\text{HCl} + 2\text{CO}_2$ and $2\text{CCl}_3\text{CHO}, \text{H}_2\text{O} + 7\text{O} = 3\text{H}_2\text{O} + 6\text{Cl} + 4\text{CO}_2$.

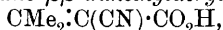
P. H.

A Soluble Polychloral. SIMON GARTNER (D.R.-P. 165984).—By treating chloral with pyridine or other amines in the cold and then acidifying the product, a stable, homogeneous polymeride of chloral is obtained, which retains the soporific action of the simple aldehydehydrate, but is less poisonous, and differs from the polychlorals previously described in dissolving in water or alcohol, slowly at the

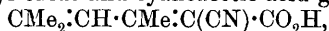
ordinary temperature and rapidly on boiling, to yield respectively chloral hydrate or chloral alcoholate.

If trimethylamine is employed to induce this polymerisation, it should be used in dilute solutions of inert solvents, otherwise the reaction is very violent and an ill-defined heterogeneous product is obtained. G. T. M.

Condensation of Ketones with Cyanoacetic and Malonic Acids. EMIL KNOEVENAGEL (D.R.-P. 162281. Compare Abstr., 1905, i, 169; also Komppa, Abstr., 1901, i, 114).—Acetone condenses with cyanoacetic acid in presence of piperidine hydrochloride on the water-bath, forming *α-cyano-ββ-dimethylacrylic acid*,



melting at 130°. Acetophenone and cyanoacetic acid give *α-cyano-β-phenyl-β-methylacrylic acid*, $\text{CPhMe:C(CN)\cdot CO}_2\text{H}$, melting at 135—136°. Mesityl oxide and cyanoacetic acid give the *acid*,



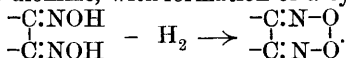
melting at 96°. When acetone and cyanoacetic acid are heated for a long time with ethylamine, carbon dioxide is evolved, and *αγ-dicyano-ββ-dimethylbutyric acid*, $\text{CN\cdot CH}_2\text{:CMe}_2\text{:CH(CN)\cdot CO}_2\text{H}$, melting at 196—197°, is formed. Acetone and malonic acid yield *ββ-dimethylacrylic acid*. C. H. D.

Behaviour of Acetoxime and of Dioximes towards Sodium Hypochloride. Properties of Carbon Tetrabromide. GIACOMO PONZIO (*Atti R. Accad. Sci. Torino*, 1906, 41, 415—426).—The action of sodium hypochlorite on acetoxime yields, not acetoxime hypochlorite, as was stated to be the case by Möhlau and Hofmann (Abstr., 1887, 795), but firstly *β-chloro-β-nitrosopropane*, which afterwards undergoes oxidation to *β-chloro-β-nitropropane*. *β-Chloro-β-nitrosopropane*,



has a pungent odour and the characteristic blue colour of nitrolic liquid compounds, and under 18 mm. pressure boils at about 7° giving a colourless vapour, whilst under the ordinary pressure it boils and decomposes at about 68°.

With sodium hypochlorite, *p*-quinonedioxime gives *p*-dinitrobenzene and *β*-naphthaquinonedioxime yields 1 : 2-dinitronaphthalene, whilst the dioximes of benzyl and of camphoquinone are transformed into the corresponding peroxides. The reaction between sodium hypochlorite and the dioximes may be regarded as the elimination of two atoms of hydrogen from the dioxime, with formation of a cyclic compound :



The mode of action of sodium hypochlorite on the dioximes is hence similar to that of potassium ferricyanide, with the advantages that the oxidation takes place almost instantaneously and in the cold, that a theoretical yield is obtained, and that the products do not require the tedious purification necessary when ferricyanide is employed.

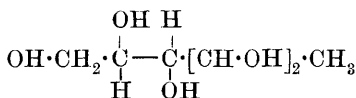
A simple method of preparing carbon tetrabromide consists in dissolving 10 grams of acetone in 10 litres of water, adding 180 grams of bromine and 1500 c.c. of a 30 per cent. solution of sodium hydroxide,

and allowing to remain. It can also be obtained by the action of sodium hypobromite on diacetyldioxime, methylethylketoxime, *iso*-nitrosomethyl ethyl ketone, or *isonitrosocamphor*. It exhibits the following reactions (compare Bolas and Groves, this Journal, 1871, 29, 782). When heated with water in a sealed tube at 200°, it is completely decomposed into carbon dioxide and hydrogen bromide, according to the equation $\text{CBr}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{HBr}$. When heated with alcohol in a sealed tube at 150°, carbon tetrabromide yields ethyl bromide, bromoform, and traces of acetaldehyde; when 80 per cent. alcohol is used, the action begins at 100°. With sodium ethoxide in ethereal solution, carbon tetrabromide gives ethyl orthocarbonate. When heated with aniline, carbon tetrabromide yields aniline hydrobromide, whilst with aniline and alcoholic potassium hydroxide solution phenylcarbylamine is obtained. Phenylhydrazine hydrobromide may be readily prepared by adding phenylhydrazine to an ethereal solution of carbon tetrabromide cooled in ice; if alcoholic potassium hydroxide is present, phenylcarbylamine is formed.

T. H. P.

Rhodeitol. EMIL VOTOČEK and J. BULÍŘ (*Zeit. Zuckerind. Böhm.*, 1906, 30, 333—339).—Rhodose, previously prepared from convolvulin (Abstr., 1900, i, 332) may be more cheaply obtained by heating powdered jalap resin (*Resina jalapae e radice ponderosa*) with barium hydroxide solution to dissolve the glucoside and leave the resin unchanged, removing the barium hydroxide, and hydrolysing by means of 10 per cent. sulphuric acid solution.

Rhodeitol, $\text{C}_6\text{H}_{14}\text{O}_5$, best prepared by reducing rhodose by means of 2.5 per cent. sodium amalgam in a solution kept alkaline to an extent not exceeding 0.5 per cent. of sodium hydroxide, crystallises from alcohol in silky, white plates melting at 153.5° and is readily soluble in water; it can be distilled, reduces Fehling's solution, and has $[\alpha]_D - 1.45^\circ$ in aqueous solution or -4.6° in 10 per cent. borax solution at 21°. Oxidation of rhodeitol by means of bromine in sodium carbonate solution or of nitric acid yields a ketose (rhodeoketose) but no aldose. Rhoditol is not oxidised by the sorbose bacterium (compare Bertrand, Abstr., 1898, i, 550), so that it must have either the formula



or the enantiomorphous one. The constitution of rhodose must hence

be represented by $\text{CHO}\cdot\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}\cdot[\text{CH}\cdot\text{OH}]_2\cdot\text{CH}_3$ or by the mirror-image

of this formula.

A mixture of equal proportions of the two optical antipodes, rhodose and fucose, gives on reduction with sodium amalgam a true racemic compound, *r-rhodeitol* or *r-fucitol*, $\text{C}_6\text{H}_{14}\text{O}_5$, which crystallises in shining plates melting at 168° and dissolves readily in water and sparingly in alcohol.

T. H. P.

The almost complete Conversion into Maltose of the Dextrins obtained by the Saccharification of Starch. AUGUSTE FERNBACH and JULES WOLFF (*Compt. rend.*, 1906, 142, 1216—1218. Compare Maquenne and Roux, this vol., i, 327).—At a temperature of 50° , starch is almost completely converted into maltose by the action of malt extract, and the second stage of the reaction, namely, the conversion of the dextrin into maltose, is accelerated by adding acid until the liquid is neutral to methyl-orange. Under these conditions, 300 c.c. of a solution containing 13 grams of starch and 50 c.c. of a 10 per cent. malt extract yielded after ninety-four hours 103.8 grams of maltose per 100 grams of starch, or 1.7 per cent. less than the theoretical quantity; the solution contained 1.9 per cent. of dextrin which had escaped saccharification owing to the dilution. If, however, the dextrin is precipitated by alcohol and then subjected to the further action of malt extract, it is slowly converted into maltose.

M. A. W.

Combinations of Mercuric Iodide and Methylamine. MAURICE FRANÇOIS (*Compt. rend.*, 1906, 142, 1199—1202. Compare Abstr., 1905, i, 574).—Mercuric iodide readily combines with gaseous methylamine at the ordinary temperature to form the liquid $5\text{NH}_2\text{Me}, \text{HgI}_2$, which by loss of methylamine forms successively the solid compounds $2\text{NH}_2\text{Me}, \text{HgI}_2$ and $\text{NH}_2\text{Me}, \text{HgI}_2$.

Pentamethylaminomercuric iodide, $5\text{NH}_2\text{Me}, \text{HgI}_2$, most conveniently prepared in a pure state by the action of methylamine on the compound, $2\text{NH}_2\text{Me}, \text{HgI}_2$, forms a colourless liquid which solidifies at -46° , can be preserved indefinitely in sealed tubes, but loses methylamine when exposed to the air, the dissociation pressure at 0° being 280 mm. and becoming atmospheric at 25° .

Dimethylaminomercuric iodide, $2\text{NH}_2\text{Me}, \text{HgI}_2$, obtained from the preceding compound by partial loss of methylamine, or by adding an excess of methylamine solution to a saturated solution of mercuric iodide in potassium iodide, forms colourless prisms sometimes 10 cm. long, with an ammoniacal odour.

Methylaminomercuric iodide, $\text{NH}_2\text{Me}, \text{HgI}_2$, is obtained from the preceding compound by subjecting it at the ordinary temperature to a current of air for twelve hours, or by placing a capsule containing a weighed quantity of the compound, $2\text{NH}_2\text{Me}, \text{HgI}_2$, in a closed vessel containing mercuric iodide, or by pouring a solution of methylamine into excess of a saturated solution of mercuric iodide in potassium iodide; the compound is a yellowish-white solid which yields red mercuric iodide on prolonged exposure to the air.

M. A. W.

Synthesis of Secondary Mixed Amines by Hinsberg's Method. A. MULDER (*Rec. trav. chim.*, 1906, 25, 104—107).—The author has prepared methylpropylamine, ethylpropylamine, and ethylisopropylamine by the general method described by Hinsberg (Abstr., 1892, i, 64). Good yields were obtained except in the case of ethylisopropylamine, and it appears that Hinsberg's method is not suited to the preparation of mixed amines containing a secondary carbon atom. *Benzenesulphonmethylpropylamide*, $\text{SO}_2\text{Ph}\cdot\text{NMePr}^a$, obtained by the action of propyl iodide on the potassium derivative of benzenesulphon-

methanamide, $\text{SO}_2\text{Ph}\cdot\text{NMeK}$, is a colourless oil and boils at $184\text{--}186^\circ$ under 21 to 24 mm. pressure. *Benzenesulphonethylpropylamide*, similarly obtained, boils at $229\text{--}231^\circ$ under 26 to 33 mm. pressure. *Benzenesulphonethylisopropylamide* is crystalline, melts at $51\text{--}52^\circ$, and is readily soluble in the usual solvents with the exception of water and light petroleum. T. A. H.

Action of Ethylenediamine on Cobalt and Platinum Compounds. HERMANN GROSSMANN and BERNHARD SCHÜCK (*Ber.*, 1906, 39, 1896—1901).—Werner and Bräunlich (*Abstr.*, 1900, i, 86), by the action of varying amounts of potassium thiocyanate on dichlorodiethylenediamine cobaltchloride, have prepared the isomerides $[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{S}\cdot\text{C}\cdot\text{N})_2]\text{Cl}$ and $[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{N}\cdot\text{C}\cdot\text{S})_2]\text{Cl}$, the existence of which depends on the tautomerism exhibited by thiocyanic acid. The authors have prepared compounds of the isothiocyanato-series by a simpler method than Werner and Bräunlich's and quite free from the isomeric thiocyanato-salts by passing air through an aqueous solution of a mixture of ethylenediamine (2 mols.) and cobalt thiocyanate (1 mol.) on a boiling water-bath until the solution becomes carmine-red. Glistening, ruby-red needles of the diisorhodanato-salt, previously described by Werner and Bräunlich, separate.

Triethylenediamine cobaltthiocyanate, $(\text{Co}, 3\text{C}_2\text{H}_8\text{N}_2)(\text{SCN})_3$, prepared by heating an aqueous solution of ethylenediamine (3 mols.) and cobalt thiocyanate (1 mol.), forms golden-yellow, glistening crystals and melts at 211° . It gives the characteristic coloration with ferric chloride. On the addition of potassium cyanide, the solution becomes yellowish-red and, on cooling, the luteocyanide separates in cubical crystals melting at 240° .

The *bromide*, $(\text{Co}, 3\text{C}_2\text{H}_8\text{N}_2)\text{Br}_3\cdot 2\text{H}_2\text{O}$, prepared by the action of ethylenediamine (2 mols.) on cobalt bromide (1 mol.), forms yellow needles and melts and decomposes at 271° .

Dibromodiethylenediamine cobaltthiocyanate, $[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2]\text{SCN}, \text{H}_2\text{O}$, prepared by the action of potassium thiocyanate on a cold saturated solution of the praseobromide, $[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2\text{Br}_2]\text{Br}$, forms green crystals, the aqueous solution of which changes from green to red when boiled with water.

The *compound*, $[\text{Pt}(\text{C}_2\text{H}_8\text{N}_2)(\text{SCN})_2](\text{SCN})_2$, prepared by the action of ethylenediamine on potassium platonic thiocyanate, $\text{K}_2\text{Pt}(\text{SCN})_6$, forms yellow crystals and melts at 141° .

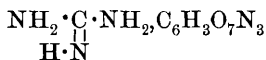
The *compound*, $[\text{Pt}(\text{C}_2\text{H}_8\text{N}_2)_2](\text{SCN})_2$, prepared in an analogous manner from potassium platinous thiocyanate, $\text{K}_2\text{Pt}(\text{SCN})_4$, forms orange-yellow crystals and melts at 177° . A. McK.

Bromodialkylacetamides. KALLE & Co. (D.R.-P. 166359).—Bromodiethylacetamide, $\text{C}_2\text{Et}_2\text{Br}\cdot\text{CO}\cdot\text{NH}_2$ or $\text{C}_2\text{Et}_2\text{Br}\cdot\text{C}(\text{NH})\cdot\text{OH}$, was prepared by adding very slowly the calculated amount of bromine to diethylacetamide dissolved in water; the product is extracted with ether recrystallised from dilute alcohol. A similar bromo-derivative was obtained from ethylpropylacetamide. G. T. M.

Hydroxymethyl Derivatives of Amides. ALFRED EINHORN (D.R.-P. 162395. Compare Abstr., 1905, i, 646; this vol., i, 245).—The method of preparation of hydroxymethyl derivatives from aromatic amides is not applicable to fatty amides unless containing substituted halogen. Thus, chloroacetamide readily reacts at 100° with formaldehyde in presence of concentrated hydrochloric acid. The product is evaporated in a vacuum after neutralising with sodium acetate, and the resulting syrup crystallised from acetone.

C. H. D.

Probable Stereoisomerism of Nitrogen in Guanidine Picrate. VICTOR VON CORDIER (*Chem. Centr.*, 1906, i, 340; from *Verh. Ges. Deut. Naturforsch. Aerzte*, 1904, ii, 105—108).—Guanidine picrate is usually obtained in the form of dark yellow plates which, owing to repeated twinning, have a hook-like structure, but when guanidine which has been prepared by the decomposition of methyl guanidine sulphate by means of barium hydroxide is used, the picrate crystallises in rosettes of bright yellow needles. Both forms have the same composition, temperature of decomposition, sp. gr., and electrical conductivity, but whilst 100 parts water dissolve 0.037 part of the plates at 0°, 0.061 at 20°, and 0.574 at 80°, the solubility of the needles is 0.043, 0.060, and 0.800 at these temperatures respectively. One form cannot be obtained from the other by crystallisation. When either is converted into the carbonate or other salt, or even into derivatives such as glycoamine, guanidinesarcosine hydrochloride, &c., and the picrate again prepared, it usually crystallises in the original form. Under certain conditions, however, it is possible to obtain the crystalline plates from the carbonate or glycine compound which has been prepared from needles of the picrate, but the reverse change has not been observed. Both forms are optically inactive, and are probably stereoisomerides, the plates being the stable modification

$$\text{NH}_2 \cdot \underset{\text{N} \cdot \text{H}}{\underset{|}{\text{C}}} \cdot \text{NH}_2, \text{C}_6\text{H}_3\text{O}_7\text{N}_3,$$


E. W. W.

Preparation of Hydrogen Cyanide from Ferrocyanides. WALTHER FELD (D.R.-P. 162362).—Sufficient calcium hydroxide or carbonate is added to a solution of calcium ferricyanide to combine with all the iron present; mercuric chloride is then added, together with magnesium chloride, to prevent the precipitation of mercuric oxide, and the whole is boiled. The reaction is $\text{Ca}_3(\text{FeCy}_6)_2 + 3\text{Ca}(\text{OH})_2 + 6\text{HgCl}_2 = 6\text{HgCy}_2 + 6\text{CaCl}_2 + \text{Fe}_2(\text{OH})_6$. The precipitate is filtered off and the solution distilled with sulphuric acid. Ferrocyanides are previously oxidised to ferricyanides with bleaching powder and sulphuric acid.

C. H. D.

Reduction of Potassium Ferricyanide. DOMENICO VENDITORI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 370—373).—Potassium ferri-

cyanide is reduced by hydrogen sulphide, slowly at the ordinary temperature, rapidly on heating, the reaction being expressed by the equation $6K_3FeCy_6 + 3H_2S = 4K_4FeCy_6 + K_2Fe_2Cy_6 + 6HCN + 3S$. These results differ from those obtained by Williamson (*Annalen*, 1846, 57, 237).

T. H. P.

Ferricyanides of Mercury, GUSTAVE FERNEKES (*J. Amer. Chem. Soc.*, 1906, 28, 602—605).—*Mercuric ferricyanide*, $Hg_3Fe_2(CN)_{12}$, obtained by adding a concentrated aqueous solution of potassium ferricyanide to a solution of mercuric chloride in alcohol and ether and washing the precipitate with alcohol and ether, is a bright yellow substance which is fairly stable when dry, but rapidly undergoes decomposition in aqueous solution with formation of hydrogen cyanide and a blue substance, which is probably Prussian blue.

Mercurous ferricyanide, $Hg_3Fe(CN)_6$, is obtained as a flocculent, cream-coloured precipitate when a solution of mercurous nitrate is added to a solution of potassium ferricyanide, and turns blue on exposure to the air.

E. G.

Oxidation of Chromous Salts. JULIUS SAND and O. BURGER (*Ber.*, 1906, 39, 1771—1779. Compare Abstr., 1903, ii, 549; 1904, ii, 39; Kohlschütter, *ibid.*, ii, 737).—When nitric oxide is passed into a moist amyl-alcoholic solution of chromous thiocyanate and excess of ammonium thiocyanate, an opaque, dark red solution is obtained which can be concentrated on the water-bath. After removal of the alcohol, the purple residue is recrystallised from hot concentrated ammonium hydroxide; it separates in glistening needles which have the composition $O[Cr(SCN)_2]_2 \cdot 4NH_3$. The ammonia is only loosely bound, being eliminated by dilute hydrochloric acid, and from the conductivity and cryoscopic behaviour of the solution the residual, $Cr_2(SCN)_4O$, functions as a binary electrolyte. Nitrous acid precipitates unstable black crystals from an ice-cold solution of the substance in dilute sulphuric acid. From a dilute hydrochloric acid solution, pyridine and water precipitate violet-grey crystals having the composition $Cr_2(SCN)_4O(C_5H_5N)_4$.

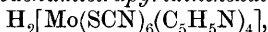
When the oxidation of the amyl-alcoholic solution of chromous thiocyanate and excess of ammonium thiocyanate is performed in the presence of pyridine by nitric oxide, ammonium persulphate, or alcoholic iodine, a very stable substance, $Cr(SCN)_4(C_5H_5N)_2 \cdot H(C_5H_5N)$, is obtained, which is not attacked by acidified hydrogen peroxide or by chlorine and boiling hydrochloric acid. With alcoholic pyridine, it forms a substance, $[Cr(SCN)_4(C_5H_5N)_2(C_5H_5N)]H(C_5H_5N)$, in harmony with the co-ordination theory.

The action of nitric oxide on chromous salts in ammonium carbonate solution leads to the formation of a basic chromammonium carbonate, $Cr(NH_4)(OH)_2CO_3$.

C. S.

Reduction of Molybdic Acid in Thiocyanic Acid Solution. JULIUS SAND and O. BURGER (*Ber.*, 1906, 39, 1761—1770. Abstr., 1905, i, 923; Chilesotti, this vol., ii, 263, 365).—Through a solution of ammonium molybdate and excess of ammonium thiocyanate in

dilute hydrochloric acid a current of 1.95 amperes is passed until two farads have been utilised for each gram-mol. of molybdic acid, the platinum cathode being smooth and of 300 sq. cm. area. The reduced liquid is treated with ether, pyridine added until the ethereal layer is colourless, the red oil is separated and boiled with alcohol. The brown, crystalline residue is described subsequently. The alcoholic solution by treatment with excess of ether deposits a yellow oil, soluble in ammonium hydroxide and reprecipitated by cold acid in yellow crystals of *molybdenumtetrapyridinehexathiocyanic acid*,



which readily loses pyridine and is best purified by precipitation from potash solution by carbon dioxide. When treated with pyridine in methyl-alcoholic solution, it yields the hexathiocyanate previously described (*loc. cit.*). After the action of hydrogen chloride on the acid in acetone, ether precipitates amber-yellow crystals of the composition $\text{Mo}(\text{SCN})_6(\text{C}_5\text{H}_5\text{N})_4\text{H}_2(\text{C}_5\text{H}_5\text{N})_2\text{HCl}$, which melt at 141° .

The *zinc*, *nickel*, and *copper* salts precipitated from ammoniacal solution contain $(\text{NH}_3)_4$ in the place of $(\text{C}_5\text{H}_5\text{N})_4$; the zinc salt, $\text{Zn}[\text{Mo}(\text{SCN})_6(\text{NH}_3)_4]$, crystallises from hot concentrated ammonium hydroxide in glistening needles and is especially characteristic. The *silver* salt, $\text{Ag}_2[\text{Mo}(\text{SCN})_6(\text{C}_5\text{H}_5\text{N})_4]$, is precipitated from methyl-alcoholic and pyridine solution in yellow crystals.

Evidence is quoted which indicates that the molybdenum in these compounds functions as a quadrivalent element.

The brown crystals previously mentioned separate from hot alcohol in aggregates of brown, feathery crystals which melt and decompose at 182° . They were previously described as having the composition $\text{Mo}[(\text{C}_5\text{H}_5\text{N})_2(\text{SCN})_4]$ (*loc. cit.*), but are now found to be $\text{Mo}(\text{OH})_2(\text{SCN})_3(\text{C}_5\text{H}_5\text{N})_2$. The chloride is $\text{MoOCl}_3(\text{C}_5\text{H}_5\text{N}, \text{HCl})_2$, not $\text{Mo}(\text{C}_5\text{H}_5\text{N}, \text{HCl})_6\text{Cl}_4$ (*loc. cit.*), and is easily hydrolysed in dilute alcohol to a basic salt, $\text{Mo}(\text{OH})_3\text{Cl}_2\text{C}_5\text{H}_5\text{N}$. The brown molybdenum-dihydroxydipyridinetriithiocyanate does not react with atmospheric oxygen; with 20 per cent. sulphuric acid, it forms a purple solution from which dark green crystals, $[\text{Mo}(\text{OH})(\text{C}_5\text{H}_5\text{N})_2(\text{SCN})_{3.12}\text{SO}_4]$, separate.
C. S.

New Methods of preparing some Organic Derivatives of Arsenic. VICTOR AUGER (*Compt. rend.*, 1906, 142, 1151—1153. Compare Abstr., 1904, i, 22, 724, 983).—Starting with methylarsonic acid or cacodylic acid, which are commercial products, the following organic derivatives of arsenic can be readily prepared: methylarsine di-iodide, AsMeI_2 , obtained by reducing methylarsonic acid with sulphur dioxide and treating the product with potassium iodide and hydrochloric acid, the yield is 82 per cent. of the theoretical, and it is converted quantitatively into methylarsine oxide, AsMeO , by heating a solution in benzene with dry sodium carbonate; methylarsine dichloride, AsMeCl_2 , prepared by adding methylarsonic acid to phosphorus trichloride, contains a small quantity of arsenic trichloride; cacodyl chloride, AsMe_2Cl , obtained with an excellent yield by distilling a mixture of sodium hypophosphite, cacodylic acid, and hydrochloric acid, $2\text{AsMe}_2\text{O}_2\text{H} + 3\text{H}_3\text{PO}_2 + 2\text{HCl} = 3\text{H}_3\text{PO}_3 + \text{H}_2\text{O} + 2\text{AsMe}_2\text{Cl}$, or

by the action of phosphorus trichloride on cacodylic acid, is converted into cacodylic oxide by the action of dry sodium carbonate; cacodyl, As_2Me_4 , is readily prepared by the action of excess of sodium hypophosphite on cacodylic acid in hydrochloric acid solution; tetramethylarsonium iodide, AsMe_4I , obtained by the action of hypophosphorus acid and methyl iodide on cacodylic acid according to the equation $\text{AsMe}_2\text{O}_2\text{H} + 2\text{MeI} + 2\text{H}_3\text{PO}_2 = \text{AsMe}_4\text{I} + 2\text{H}_3\text{PO}_3 + \text{HI}$.

M. A. W.

Preparation and Properties of Individual Organo-magnesium Compounds. WLADIMIR TSCHELINZEFF (*Chem. Zeit.*, 1906, 30, 378—379. Compare this vol., ii, 334, 335).—Magnesium alkyl compounds of the type $\text{R}\cdot\text{Mg}\cdot\text{R}$ are solid substances which decompose on heating without melting; they are soluble in a mixture of ether and benzene, and can be recovered from this solution unchanged. They catch fire and explode in contact with water, carbon dioxide, or oxygen, and react with ketones, aldehydes, or esters to form complex substances which are decomposed by water with the formation of hydrocarbons. Compounds of the type RMgI are solids which dissolve in ether or a mixture of ether and benzene, but cannot be recovered from the solution; they react less violently with water, carbon dioxide, or oxygen, and with ketones, aldehydes, or esters they yield compounds which do not evolve hydrocarbons on treatment with water.

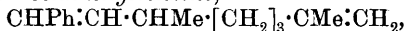
P. H.

Problem of Substitution in the Benzene Ring. ARNOLD F. HOLLEMAN (*Chem. Centr.*, 1906, i, 457—459; from *Chem. Weekblad*, 3, 1—11. Compare Abstr., 1903, i, 336, 623; 1904, i, 486; 1905, i, 41, 42, 515).—The problem of substitution in the benzene ring is discussed at length in the abstract, and some of the work of the author published already on the nitration of benzene derivatives is quoted. For further details, the abstracts or original paper should be consulted.

E. W. W.

Optically Active Benzene Hydrocarbons. III. AUGUST KLAGES and RICHARD SAUTTER (*Ber.*, 1906, 39, 1938—1942. Compare Abstr., 1904, i, 302; 1905, i, 579).— α -Hydroxy- $\gamma\gamma$ -dimethyl- Δ^7 -octenylbenzene, $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CHMe}\cdot[\text{CH}_2]_3\cdot\text{CMe}\cdot\text{CH}_2$, prepared by the action of acetic acid and ice on the product of the reaction of magnesium phenyl bromide with citronellaldehyde, is a colourless oil, which boils at 174° under 9.5 mm. pressure, has a sp. gr. 0.9469 at $15.5^\circ/4^\circ$, n_D 1.5137 at 15.5° , and $[\alpha]_D -1.56^\circ$ at 15.5° . The carbinol obtained on treatment of the reaction product with ice only has a higher specific rotation.

$\gamma\gamma$ -Dimethyl- Δ^7 -octadienylbenzene,



is formed by treating the carbinol with hydrogen chloride in ethereal solution cooled by ice, and heating the dichloride, $\text{C}_{16}\text{H}_{24}\text{Cl}_2$, so formed, which has n_D 1.5168 and $[\alpha]_D -9.06^\circ$ at 11.5° , with pyridine for five hours. It is a colourless, odourless, strongly refracting oil, which boils at 152° under 9.5 mm. pressure, has a sp. gr. 0.8947 at $17^\circ/4^\circ$,

n_D 1.5276, and $[\alpha]_D$ - 65.11° at 17°, and reacts with bromine in the cold, forming an oily *tetrabromide*, $C_{16}H_{22}Br_4$, together with small amounts of bromo-derivatives.

When heated with oxalic acid, the carbinol yields 1-phenyl-5-methyl-2-isopropenylcyclohexane, $C_6H_9MePh \cdot CMe:CH_2$; this is obtained as a colourless, mobile oil, which boils at 139—140° under 10 mm. pressure, has a sp. gr. 0.9462 at 15.7°/4°, n_D 1.5802, and $[\alpha]_D$ + 17°.

$\gamma\gamma$ -Dimethyl- Δ^8 -octenylbenzene, $C_{16}H_{24}$, is formed by reduction of $\gamma\gamma$ -dimethyl- Δ^8 -octadienylbenzene by means of sodium and alcohol, boils at 145—146° under 9.5 mm. pressure, has a sp. gr. 0.8844 at 11.5°/4°, n_D 1.5029, and $[\alpha]_D$ - 7.26°.

$\gamma\gamma$ -Dimethyloctylbenzene, $C_{16}H_{26}$, prepared by reducing the preceding substance with hydriodic acid and red phosphorus in a sealed tube at 160°, is obtained as a colourless, miscible oil which boils at 275° (corr.) or at 140° under 8.5 mm. pressure, and has a sp. gr. 0.8789 at 10.5°/4°, n_D 1.4960, and $[\alpha]_D$ - 1.82° at 10.5°. When treated with sulphuric acid containing 6 per cent. of sulphuric anhydride, it yields an oily *sulphonic acid*, which is soluble in water, and with sodium chloride gives a voluminous precipitate of the *sodium* salt. G. Y.

Bromination of Toluene. F. H. VAN DER LAAN (*Chem. Centr.*, 1906, i, 661—662; from *Chem. Weekblad*, 1906, 3, 15—21).—The author has made quantitative measurements with a view to determining the influence of temperature, of bromine carriers, or of light on the yield of *o*- or *p*-bromotoluene or benzyl bromide. Below 17°, no benzyl bromide is formed, whereas above 83° it is formed exclusively. Antimony tribromide only slightly increases the yield of ring-substituted derivatives, and appears rather to favour the formation of the *para*-form. Five mg. of aluminium added to 3 c.c. of bromine completely prevent the formation of benzyl bromide, and increase the yield of the *o*-variety as compared to the *p*-, whereas 2 mg. of aluminium are without effect. Ferric bromide has a similar although rather more marked effect than aluminium bromide. The action of aluminium amalgam is similar to that of aluminium bromide. The addition of 0.02 mol. of phosphorus pentabromide to 1 mol. of bromine gives, at 50°, 10 per cent. more benzyl bromide than in the absence of a halogen carrier. In diffused daylight, bromination takes place more rapidly. A reaction which at 25° is not completed in the dark after a week, is effected in ten minutes in daylight. Benzyl bromide is formed in this case, together with small quantities of more highly brominated derivatives. Pure benzyl bromide is obtained by dropping bromine into eight times its weight of toluene kept at 80°. P. H.

Preparation of Aromatic Sulphonamates by Reduction of Nitro-derivatives with Sodium Hyposulphite. ALPHONSE SEYEWETZ and BLOCH (*Compt. rend.*, 1906, 142, 1052—1054).—A mixture of nitrobenzene (63 grams), trisodium phosphate (75 grams), and sodium hyposulphite (380 grams) is made, and to it a litre of boiled water is added, and the whole vigorously shaken for some minutes and then set aside. After twenty-four hours, a quantity of sodium phenylsulphonamate will have separated; a second fraction

may be obtained by cooling the mother liquor to 0° , and a third by then evaporating the mother liquor to dryness and extracting the residue with alcohol. The yield of the sodium salt is about equal to that of the nitrobenzene taken. The process is also applicable to the preparation of the corresponding sulphonamates from the three nitrotoluenes, *m*-nitro-xylene, and α -nitronaphthalene. T. A. H.

Additive Compounds of Aromatic Hydrocarbons with Polynitro-derivatives. GIUSEPPE BRUNI and L. FERRARI (*Chem. Zeit.*, 1906, 30, 568—569).—The authors have prepared additive compounds of diphenyl, diphenylmethane, triphenylmethane, dibenzyl, stilbene, tolane, and azobenzene with picryl chloride, and find that the number of molecules of the latter compound which combines with one molecule of the hydrocarbon is proportional to the number of benzene rings contained in the hydrocarbon. P. H.

Constitutional Formula of 1:2-Dinitrosonaphthalene. GIACOMO PONZIO (*Atti R. Accad. Sci. Torino*, 1906, 41, 588—591).—Contrary to the statement of Koreff (*Abstr.*, 1886, 363), 1:2-dinitrosonaphthalene can be reduced by means of tin and hydrochloric acid, yielding naphthafurazan (Goldschmidt and Schmidt, *Abstr.*, 1884, 1359) and 1:2-naphthylenediamine. The author hence regards 1:2-dinitrosonaphthalene as β -naphthaquinonedioxime peroxide, $C_{10}H_6 \begin{smallmatrix} N \cdot O \\ \llcorner \\ N \cdot O \end{smallmatrix}$.

Oxidation of this compound in concentrated sulphuric acid solution by means of nitric acid of sp. gr. 1.52 yields the *dinitro*-derivative, $C_{10}H_4(NO_2)_2 \cdot N_2O_2$, which crystallises from acetic acid in yellow prisms melting at 212° , is moderately soluble in ethyl acetate or nitric acid, and dissolves in alkali solution, giving a red coloration.

T. H. P.

Synthesis of Alkyl Derivatives of 2:4-Dinitroaniline and of Two *iso*Propyl-2:4:6-Trinitroanilines. A. MULDER (*Rec. trav. chim.*, 1906, 25, 108—116).—The author prepared a number of these alkyl derivatives by Clemm's method (*J. pr. Chem.*, 1869, 108, 320, and 1870, ii, 1, 170), which consists in treating 1-bromo-2:4-dinitrobenzene with the appropriate amine. Negative results, however, were obtained with diisopropylamine and ethylisopropylamine, due probably to the influence of the secondary carbon atom in the *isopropyl* groups.

2:4-Dinitromethylpropylaniline, $C_6H_3(NO_2)_2NPr^aMe$, obtained by the action of methylpropylamine on the bromodinitrobenzene, forms bright yellow, prismatic crystals, melts at $71-72^{\circ}$, and is readily soluble in acetone or warm alcohol. 2:4-Dinitroethylpropylaniline, prepared similarly, separates from methyl alcohol in small, flattened, prismatic, yellow crystals and melts at $54-55^{\circ}$. 2:4-Dinitrophenylbenzylmethylamine crystallises from hot alcohol in bright yellow spangles, melts at $143-144^{\circ}$, and is readily soluble in benzene, acetone, or warm alcohol, less so in chloroform or ether. 2:4-Dinitrophenylbenzylethylamine separates from ether in large, bright yellow, transparent crystals and melts at $72-73^{\circ}$ (compare Schultz, Rohde,

and Bosch, Abstr., 1904, i, 992). 2:4-Dinitrophenylbenzylamine separates from a mixture of acetone and alcohol in small, bright yellow, prismatic crystals and melts at 115—116°. 2:4-Dinitrophenyldibenzylamine melts at 104—105° (compare Pinnow and Wiskott, Abstr., 1899, i, 501). 2:4-Dinitrophenylethylaniline melts at 95° (compare Deletra and Ullmann, Abstr., 1904, i, 272). 2:4-Dinitrophenylbenzylaniline, obtained by heating in a closed vessel at 100°, a mixture of 1-bromo-2:4-dinitrobenzene, benzylaniline, and sodium acetate in presence of alcohol, forms small, red crystals from warm acetone and melts at 168°.

2:4-Dinitrophenylpropylaniline is best prepared by heating propylaniline, obtained by Pictet and Crepieux's method (Abstr., 1888, i, 688), with bromodinitrobenzene, dissolved in alcohol, under pressure. It crystallises in brown spangles with a green sheen or in small needles of the same tint, and melts at 73—74°.

When diisopropylamine reacts with bromodinitrobenzene dissolved in alcohol, four products are formed: (1) bright yellow needles melting at 81°, (2) orange prisms melting at 106—107°, (3) prisms resembling those of No. 2, but melting at 89—90°, and (4) yellow spangles melting at 123°. None of these substances can be the 2:4-dinitrodiisopropylaniline expected.

Ethyl isopropylamine reacts very slowly with an alcoholic solution of bromodinitrobenzene, yielding an oil from which no well-defined amine can be isolated. When this oil is treated with picryl chloride, it furnishes 2:4:6-trinitroethylisopropylaniline, which exists in two forms: (1) red needles, and (2) yellow spangles. The first form passes into the second at 90°, and the latter melts at 108—109°.

2:4-Dinitroisopropylaniline crystallises in large, flattened, yellow needles from acetone, and in spangles from warm alcohol, and melts at 94—95°. When added to warm nitric acid of sp. gr. 1.52 and the solution boiled, this substance is converted into van Romburgh's 2:4:6-trinitrophenylisopropylnitroamine, which melts at 107° (compare Abstr., 1886, i, 455).

2:4:6-Trinitroisopropylaniline crystallises from a mixture of alcohol and acetic acid in yellow needles and melts at 106—107°.

T. A. H.

Oxidation of 2:4-Dinitroanilines with Chromic Anhydride.

A. MULDER (*Rec. trav. chim.*, 1906, 25, 117—120).—Van Romburgh has shown that when 2:4-dinitrodialkylanilines, dissolved in acetic acid, are oxidised with chromic acid, the alkyl groups are successively replaced by hydrogen atoms, and that when two different alkyl groups are present only one of the two possible dinitroalkylanilines is formed (Abstr., 1889, 971; 1896, i, 478). The author oxidised several of the 2:4-dinitrodialkylanilines described in the preceding abstract by van Romburgh's method and found that in most cases in addition to dinitroaniline both possible dinitromonoalkylanilines were produced, although usually one was formed in much larger quantity than the other.

2:4-Dinitrophenyldibenzylamine, on oxidation by chromic acid in presence of acetic acid, yielded 2:4-dinitrophenylbenzylamine in

addition to dinitroaniline, and not the latter only, as Pinnow and Wiskott assert (Abstr., 1899, i, 500). T. A. H.

Hexanitrodiphenylamines. A. MULDER (*Rec. trav. chim.*, 1906, 25, 121—123).—When 2:4-dinitrophenylmethylaniline is added to nitric acid of sp. gr. 1.49, and, after the first violent action has subsided, the solution is heated to the boiling point for fifteen minutes, *hexanitrodiphenylmethylaniline* is formed. This crystallises from acetic acid in small, yellow spangles and melts at 236—237°, and when boiled with an aqueous solution of potassium hydroxide yields methylamine. *Hexanitrodiphenylethylaniline*, obtained in a similar manner, forms small, colourless needles, becomes brown on exposure to light, and melts at 198—200°. It yields ethylamine when boiled with an aqueous solution of potassium hydroxide, but is resistant to chromic acid, yielding, with the latter, only a small quantity of resinous products. *Hexanitrodiphenylpropylaniline* forms small, bright yellow needles and melts at 136—137°. These three substances all give intense red colorations with alkalis. T. A. H.

Hydrogen Phosphites of Primary Cyclic Amines. PAUL LEMOULT (*Compt. rend.*, 1906, 142, 1193—1195).—When phosphorus trichloride (1 mol.) and aniline (6 mols.) are mixed in ethereal solution, aniline hydrochloride is precipitated, and the resulting mother liquor slowly absorbs water from the air and deposits voluminous white crystals of the acid phosphite of the base; the same product is obtained if chloroform is used as a solvent instead of ether, and the hydration is hastened by warming the solution at 100°. The hydrogen phosphites of the primary cyclic amines are insoluble in ether, chloroform, or benzene, but can be recrystallised from alcohol; they have definite melting points, but decompose at a slightly higher temperature with the formation of the primary base, hydrogen phosphide, and ortho-phosphoric acid. *Hydrogen aniline phosphite*, $C_6H_5 \cdot NH_2 \cdot H_3PO_3$, forms beautiful pale red or green needles, or large, brilliant crystals which melt at 179°, and is precipitated by alcohol from aqueous solution in the form of small plates melting at 179°. *Hydrogen o-toluidine phosphite*, $C_7H_7 \cdot NH_2 \cdot H_3PO_3$, forms beautiful, colourless needles which melt at 174° and decompose at 200°. *Hydrogen as-m-xylidine phosphite*, $C_8H_9 \cdot NH_2 \cdot H_3PO_4$, crystallises in colourless needles and melts at 172°. M. A. W.

Formation of Salts of Aromatic Bases with Dicarboxylic Acids. OTTO ANSELMINO (*Chem. Centr.*, 1906, i, 753; from *Ber. Deut. pharm. Ges.*, 15, 422—426. Compare Abstr., 1904, i, 306).—The results of experiments on the behaviour of oxalic and succinic acids towards a further series of aromatic bases have not indicated any regularity either in reference to the possibility of the formation of salts or to the stability of the salts. *o*-Anisidine and *m*-nitroaniline form acid oxalates; *as-m*-xylidine and *o*- and *m*-aminobenzoic acids, normal oxalates and aniline, *o*-, *m*-, and *p*-toluidines, *p*-anisidine, *p*-phenetidine, *ψ*-cumidine, *p*-aminobenzoic acid, and α - and β -naphthylamines yield both acid and normal oxalates. The acid reaction of the

acid oxalates of *m*- and *p*-toluidines is not affected by boiling with alcohol, but the acid oxalates of aniline, *o*-toluidine, *p*-anisidine, *p*-phenetidine, *p*-aminobenzoic acid, and of α - and β -naphthylamines become neutral; the acid oxalates of *o*-toluidine, *o*-anisidine, *o*-aminobenzoic acid, *m*- and *p*-nitroaniline, and of α - and β -naphthylamine form condensation products.

Aniline, *o*- and *p*-toluidine, *o*- and *p*-anisidine, *as-m*-xylidine, and β -naphthylamine form acid succinates.

o-Toluidine oxalate melts at 167°, *o*-toluidine hydrogen oxalate at 171°, *as-m*-xylidine oxalate at 167°, ψ -cumidine oxalate at 183°, ψ -cumidine hydrogen oxalate at 179°, *m*-aminobenzoic acid oxalate at 246°, *p*-aminobenzoic acid hydrogen oxalate above 275°, *p*-aminobenzoic acid oxalate above 275°, *p*-phenetidine oxalate at 201°, *p*-phenetidine hydrogen oxalate at 201°, β -naphthylamine oxalate at 181°, and β -naphthylamine hydrogen oxalate at 176°.

o-Toluidine oxalo-*o*-toluidate, $C_{16}H_{18}O_3N_2$, melts at 153°; oxalo-*o*-anisic acid, $C_8H_9O_4N$, at 159°; *m*-nitro-oxanilic acid, $C_8H_6O_5N_2$, at 158°, and ethyl *p*-nitro-oxanilate, $C_{10}H_{10}O_5N_2$, at 168°. β -Naphthylamine β -naphthylloxamate, $C_{22}H_{22}O_3N_2$, is also a condensation product.

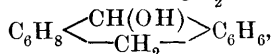
E. W. W.

Influence of Catalysts on the Formation of Anilides. II.

NICOLAI A. MENSCHUTKIN (*Chem. Centr.*, 1906, i, 551; from *Iswiestja Petersburg Polytechn. Inst.*, 1905, 4, 181—190. Compare Abstr., 1903, i, 813).—The accelerating influence of hydrogen chloride, bromide, or iodide on the rate of acetylation of aniline, *o*-, *m*-, or *p*-toluidine, and *m*- or *p*-xylidine by acetic acid was found to be proportional to the molecular weight of the acid and to the quantity employed. In the presence of these acids, the reaction was uni-molecular, otherwise it was bi-molecular. A methyl group in the ortho-position decreases the velocity of acetylation, whereas in the meta- or para positions it increases it.

P. H.

Some Hydroanthracene Derivatives. MARCEL GODCHOT (*Compt. rend.*, 1906, 142, 1202—1204. Compare Abstr., 1904, i, 987; 1905, i 201).—Octahydroanthranol, $C_6H_{10}\begin{smallmatrix} \text{CH(OH)} \\ \text{CH}_2 \end{smallmatrix}C_6H_4$ or



obtained by reducing hexahydroanthrone by means of sodium and alcohol, crystallises in small, yellow needles, melts at 81—82°, is very soluble in the ordinary solvents, and loses H_2O on distillation even in a vacuum to form a hexahydroanthracene; the *phenylurethane*, $C_{14}H_{17}O \cdot CO \cdot NHPh$, crystallises from acetone in beautiful, colourless needles which melt at 151—152°.

β -Hexahydroanthracene, isomeric with the compound described by Graebe and Liebermann (Abstr., 1882, 857), obtained from octahydroanthranol either by distillation or by boiling it in alcoholic solution with a few drops of hydrochloric acid, or by heating it with acetic or benzoic anhydride or chloride, crystallises in small, colourless plates;

it melts at 66.5° , boils at $303-306^{\circ}$, is insoluble in water, soluble in hot alcohol, acetic acid or benzene, the solutions exhibiting a beautiful blue fluorescence. It yields dihydro-oxanthranol on oxidation, and reacts with chlorine or bromine to form dichloro- or dibromo-octahydroanthracene identical with the compounds similarly obtained from octahydroanthracene (Abstr., 1904, i, 987); β -hexahydroanthracene has therefore the formula $C_6H_{10} \begin{smallmatrix} \text{CH} \\ | \\ \text{CH} \end{smallmatrix} C_6H_4$ or $C_6H_8 \begin{smallmatrix} \text{CH} \\ | \\ \text{CH} \end{smallmatrix} C_6H_6$.

9 : 10-*Tetrahydroanthracene*, $C_6H_6 \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix} C_6H_4$, obtained by reducing dihydro-oxanthranol by means of hydrogen iodide, forms colourless plates which melt at 101° , is readily soluble in the ordinary reagents, and the solutions are not fluorescent; it yields dihydro-oxanthranol on oxidation, and readily forms substitution products with chlorine or bromine. 9 : 10-*Dibromotetrahydroanthracene*, $C_6H_6 \begin{smallmatrix} \text{CHBr} \\ | \\ \text{CHBr} \end{smallmatrix} C_6H_4$, crystallises in large, yellow needles, melts at 169° , and is not attacked by aqueous or alcoholic potassium hydroxide at 250° .

M. A. W.

Phenol. HUGO KÜHL (*Chem. Centr.*, 1906, i, 344—345; from *Pharm. Zeit.*, 50, 1001).—When phenol which has been kept for a long time and has become red is distilled, a solid, violet-red residue remains, which is insoluble in water or ammonia. By the action of hydrogen peroxide on an ammoniacal solution of phenol, a green coloration is formed after some time. No characteristic coloration is formed when sodium nitrite is added to a solution of phenol in concentrated sulphuric acid. When heated with a solution of ferric chloride and evaporated on the water-bath, a residue is left which has a faint red tinge.

E. W. W.

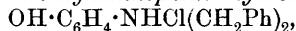
Aluminium Phenoxide. ALFRED N. COOK (*J. Amer. Chem. Soc.*, 1906, 28, 608—617).—A method is described for the preparation of aluminium phenoxide, $Al(OPh)_3$ (Gladstone and Tribe, *Trans.*, 1882, 41, 5). The compound is a grey, translucent, brittle solid which melts at 265° , has a vitreous lustre, a sp. gr. 1.23, and is soluble in hot benzene, toluene, or xylene, and also in dry alcohol, chloroform, carbon disulphide, or acetone. The compound is decomposed by water with formation of aluminium hydroxide. It reacts with bromine with production of tribromophenol bromide. When aluminium phenoxide is treated with nitric acid, *o*-nitrophenol, 1 : 2 : 4-dinitrophenol, and picric acid are produced. The substance reacts with alcohol with formation of aluminium ethoxide and phenol, and also with ether with production of aluminium ethoxide and phenetole. The action of several other reagents is described. Aluminium phenoxide is decomposed by heat with formation of benzene, phenol, phenyl ether, and some higher boiling substances which have not been identified. This decomposition affords a good method for the preparation of phenyl ether.

E. G.

5-Nitro-2-aminophenol. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 165650).—5-Nitro-2-aminophenol is readily obtained by dissolving ethenyl-*o*-aminophenol in cold concentrated sulphuric acid and nitrating with a mixture of this acid and nitric acid. The nitroethyl-*o*-aminophenol thus produced is boiled with an equal weight of hydrochloric acid until solution is complete, when 5-nitro-2-aminophenol is precipitated on neutralising the solution with sodium or calcium carbonate. G. T. M.

Action of Benzyl Chloride on Aminophenols. MARUSSIA BAKUNIN (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1905, [iii], 11, 361—375).—When *p*-aminophenol and benzyl chloride are heated together in alcoholic solution in presence of zinc, an organo-zinc chloro-compound melting at 240° is obtained, which, on decomposition with water, gives rise to benzylaminophenol hydrochloride melting at 224°.

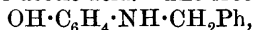
The interaction of *p*-aminophenol and benzyl chloride in alcoholic solution yields: (1) *p*-dibenzylaminophenol hydrochloride,



which crystallises from alcohol in short, colourless, monoclinic prisms melting at 200—224°, and is almost insoluble in the ordinary organic solvents; water dissolves it and liberates the free base, a decomposition more readily effected by dilute sodium hydroxide or carbonate solution, or by the action of metallic zinc on the alcoholic solution. (2) A small quantity of *p*-benzylaminophenol hydrochloride,



which crystallises from water in long, glassy prisms containing H_2O , and melts in its water of crystallisation at 130° and afterwards at 172°; it is soluble in alcohol or acetic acid. The free base,



separates from alcohol or water in nacreous laminæ melting at 89—90° and dissolves in benzene or chloroform.

The interaction of *o*-aminophenol and benzyl chloride yields: (1) *o*-dibenzylaminophenol hydrochloride, $\text{C}_{20}\text{H}_{19}\text{ON} \cdot \text{HCl}$, which crystallises from water or alcohol in regular octahedra melting at 200—205°; (2) *o*-benzylaminophenol hydrochloride; the free base crystallises from light petroleum in nacreous laminæ melting at 81—82°. T. H. P.

Action of Iodine Chloride on Catechol. C. LORING JACKSON and M. C. BOSWELL (*Amer. Chem. J.*, 1906, 35, 519—531).—The experiments described were carried out with the object of preparing tetraiodo-*o*-benzoquinone.

By the action of iodine chloride (270 grams) on catechol (30 grams), a dark red mass is produced containing a large quantity of iodine. On removing the iodine by means of potassium iodide solution, a substance, probably octachlorotri-iodopentacatechol, $\text{C}_{20}\text{H}_{19}\text{O}_{10}\text{Cl}_8\text{I}_3$, is obtained, which crystallises from dilute alcohol in long, white, silky needles, melts at 224°, and is soluble in ether, benzene, or acetic acid; its diacetyl derivative was prepared. This compound is converted by nitric acid into a dark red substance, which crystallises from toluene in long, bright red needles, becomes darker on drying, owing

probably to loss of toluene of crystallisation, and then melts at 272° ; it tends to become light yellow when treated with benzene, light petroleum, or dilute acetic acid.

If the iodine is not removed from the product of the reaction before treatment with sulphur dioxide, trichlorocatechol is produced, which crystallises with H_2O and melts at 115° instead of $104\text{--}105^{\circ}$, as stated by Cousin (Abstr., 1895, i, 456).

If 30 grams of catechol are treated with 360 grams of iodine chloride, a compound is obtained, probably *heptachloroiidotricatechol*, $\text{C}_{18}\text{H}_{10}\text{O}_6\text{Cl}_7\text{I}$, which crystallises from hot dilute alcohol in long, white, silky needles, melts at 252° , and is soluble in alcohol or acetic acid; its *diacetyl* derivative was prepared.

If in preparing this compound the reduction with sulphur dioxide is effected before removing the iodine, tetrachlorocatechol (m. p. $194\text{--}195^{\circ}$) is produced, which crystallises with H_2O .

Indications have been obtained that by varying the proportion of iodine chloride another compound may be obtained which melts at 270° .

Attempts were made by other methods to prepare tetraiodocatechol or tetraiodo-*o*-quinone, but without success. E. G.

Phloroglucinol. MAXIMILIAN NIERENSTEIN (*Chem. Centr.*, 1906, i, 553; from *Collegium*, 1906, 14—15).—Phloroglucinol, when treated in ethereal solution with diazomethane, gives an almost quantitative yield of an enolic ether melting at 52.5° , and it is therefore suggested that diazomethane might be a useful reagent for the study of tautomeric modifications. Both resorcinol and pyrogallol give the pine shaving reaction which hitherto has been supposed to be characteristic of phloroglucinol. P. H.

Preparation of Dialkylmalonyl-*p*-phenetidines. AKTIENGESellschaft FÜR ANILIN-FABRIKATION (D.R.-P. 165311).—Dialkylated malonylphenetidines are obtained by the interaction of 2 mols. of phenetidine and 1 mol. of dialkylmalonyl chloride, the former reagent being dissolved in benzene. Clinical experiments have shown that in addition to their antipyretic properties these dialkylmalonyl-*p*-phenetidines have also a saporific action.

Diethylmalonyl-p-phenetidine, $\text{CET}_2(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$, crystallises from alcohol in white needles melting at 186° ; it is sparingly soluble in hot water, but dissolves readily in hot alcohol or benzene.

Dipropylmalonyl-p-phenetidine, $\text{CPr}^a_2(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$, resembles the preceding compound and melts at 143° . G. T. M.

Preparation of Aromatic Alcohols and their Ethers by the Electrolytic Reduction of Aromatic Esters. CARL METTLER (D.R.-P. 166181).—The carboxyl group of an aromatic ester can be reduced electrolytically when the metal chosen for cathode has a high supertension, lead being the best metal for the purpose. It is necessary also to have a solvent which can conduct the electric current, and concentrated sulphuric acid is found convenient since it may be diluted with water, alcohol, or glacial acetic acid; this solvent may,

however, be replaced by an aqueous-alcoholic solution of phosphoric or hydrochloric acid. Under these conditions the alkyl esters of benzoic acid and its derivatives are reduced, yielding a mixture of the corresponding alcohol and its alkyl ether; the proportion of the two products depends on the constitution of the original ester. In alkaline solutions the alcohol alone is produced. These alcohols and their ethers are readily oxidised to the technically important aromatic aldehydes.

Ethyl benzoate when electrolysed in the cathode cell with a current density of 7 amperes per 100 sq. cm. at 20—30° yielded a mixture of benzyl alcohol and benzyl ethyl ether; the solvent in this case was a mixture of dilute sulphuric acid and alcohol. With this solvent and at a temperature of 60—80°, phenyl benzoate gave rise to a mixture of benzyl alcohol and phenyl benzyl ether. Ethyl *m*-bromobenzoate furnished *m*-bromobenzyl ethyl ether and a small amount of *m*-bromobenzyl alcohol. Benzyl benzoate yielded benzyl alcohol and dibenzyl ether.

In presence of aqueous-alcoholic ammonia, ethyl benzoate on electrolysis furnished only benzyl alcohol. G. T. M.

Benzyl *iso*Valerate. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 165897).—*Benzyl isovalerate*, $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CO}_2 \cdot \text{CH}_2\text{Ph}$, is an ester having valuable therapeutic properties, being a sedative which has no harmful effect on the mucous membrane of the stomach. It is prepared by heating together benzyl chloride and sodium *isovalerate* for ten hours at 160° and purified by fractionation under diminished pressure. The ester which has a pleasant odour and boils at 136° under 25 mm. pressure, can also be prepared by the following processes: the interaction of benzyl alcohol and *isovaleryl* chloride either in pyridine-benzene solution or in the presence of concentrated sulphuric or hydrochloric acid; the condensation of benzyl alcohol and carbonyl chloride in quinoline solution and the interaction of the resulting benzyl chlorocarbonate with sodium *isovalerate* at 160°; the direct condensation of *isovaleric* anhydride and benzyl alcohol at 180—200°. G. T. M.

Unsymmetrical Diphenylethylene Oxide. AUGUST KLAGES and JOHANNES KESSLER (*Ber.*, 1906, 39, 1753—1756. Compare *Abstr.*, 1905, i, 523; Tiffeneau and Fourneau, *Abstr.*, 1905, i, 523, 591; this vol., i, 20).—as-*Diphenylchlorohydrin* [*diphenylchloromethyl carbinol*], $\text{OH} \cdot \text{CPh}_2 \cdot \text{CH}_2\text{Cl}$, obtained by the interaction of magnesium phenyl bromide (3 mols.) and ethyl chloroacetate (1 mol.) with subsequent decomposition of the product by cold water, melts at 66°, and its vapour has an irritating action on the eyes. It reacts with diethylamine at 100° to give a poor yield of *diphenyldiethylaminomethylcarbinol*, $\text{NEt}_2 \cdot \text{CH}_2 \cdot \text{CPh}_2 \cdot \text{OH}$, which melts at 49°, and a substance which melts at 154—155° and does not contain nitrogen.

as-*Diphenylethylene oxide*, $\begin{array}{c} \text{CPh}_2 \\ | \\ \text{CH}_2 \end{array} \text{>O}$, obtained from the chlorohydrin and sodium ethoxide, is a colourless substance which melts at 56°, turns yellow in the air, and slowly becomes resinous; its vapour

has a pungent odour and is volatile in steam. The sodium hydrogen sulphite compound is decomposed by boiling dilute sulphuric acid or potassium carbonate with the formation of diphenylacetaldehyde, of which the *semicarbazone* melts at 160° , the *azine* at 165° , and the *benzoylhydrazone* at 182° . C. S.

Further Investigations of the Two Chlorides of *o*-Sulphobenzoic Acid. PHILIP H. COBB (*Amer. Chem. J.*, 1906, 35, 486—508).—Experiments on the action of hydrochloric acid on organic anhydrides have led to the conclusion that the formation of symmetrical ester chlorides by the action of alcohol on the more fusible chloride of *o*-sulphobenzoic acid is not dependent on the presence of hydrochloric acid. It has been found that the anhydrides of certain dibasic acids do not react with dry hydrogen chloride, whilst those of monobasic acids are easily attacked.

The action of alcohols and alkyl oxides on the chlorides has been studied by Bird (*Abstr.*, 1903, i, 822). The product obtained by the action of methyl alcohol on the more fusible chloride melts at 63 – 64° . The barium salt containing about 28 per cent. of barium which was obtained by Bird from the product formed by boiling either the less fusible or more fusible chloride with 95 per cent. ethyl alcohol is probably a mixture of salts of *o*-sulphobenzoic acid and the ester acid. Sodium ethoxide reacts with both chlorides with formation of diethyl *o*-sulphobenzoate in each case.

By the action of benzene on the chlorides in presence of aluminium chloride, Remsen and Saunders (*Abstr.*, 1895, i, 474) and List and Stein (*Abstr.*, 1898, i, 584) obtained *o*-benzoyldiphenylsulphone together with a product which melts at 162 – 163° and was regarded as the lactone, $C_6H_4 \begin{smallmatrix} \text{CPh}_2 \\ \text{SO}_2 \end{smallmatrix} O$. It is now considered probable that this product is not the supposed lactone.

By the action of thionyl chloride on dipotassium *o*-sulphobenzoate, *o*-sulphobenzoic anhydride is obtained together with a small quantity of the salt, $COCl \cdot C_6H_4 \cdot SO_3K$, but no *o*-sulphobenzoic chloride could be isolated. By the action of thionyl chloride on the acid potassium salt, the anhydride can be obtained in an 80 per cent. yield.

When the anhydride is heated with phosphorus oxychloride at 125° for fourteen hours, the more fusible chloride is produced.

By the action of magnesium phenyl bromide on the less fusible chloride, the substance $SO_2Ph \cdot C_6H_4 \cdot CPh_2 \cdot OH$ is obtained, which crystallises from alcohol, melts at 183 – 184° , and gives a dark red coloration with concentrated nitric and sulphuric acids. The same substance can be obtained by treating *o*-benzoyldiphenylsulphone with magnesium phenyl bromide. Magnesium phenyl bromide reacts with *o*-sulphobenzoic anhydride with formation of the compound melting at 163° , which is obtained by the action of benzene on the less fusible chloride in presence of aluminium chloride. E. G.

Preparation of Methylenehippuric Acid. CHEMISCHE FABRIK AUF AKTIEN FORM. E. SCHERING (D.R.-P. 163238. Compare *Abstr.*, 1904, i, 413).—Hippuric acid reacts with chloromethyl alcohol or the

less volatile fractions containing hydroxymethylene chlorides (Litterscheid, Abstr., 1901, i, 443) to form methylenehippuric acid. There is less formation of resin than when formaldehyde and an acid are employed.

C. H. D.

[Crystallographic Measurements of] Derivatives of Phenylcarbamic Acid. F. M. JAEGER (*Zeit. Kryst. Min.*, 1906, 42, 25—33).—Methyl phenylcarbamate crystallises from alcohol in colourless, rectangular leaflets which melt at 47° and belong to the bipyramidal class of the rhombic system [$a:b=1.5952:1$]; it has a sp. gr. 1.251 at 19°.

Methyl phenylmethylcarbamate separates from alcohol in large, colourless crystals which melt at 44° and belong to the bipyramidal class of the rhombic system [$a:b:c=0.8406:1:0.3320$]; sp. gr. 1.296 at 19°.

Methyl 4-nitrophenylmethylcarbamate separates from alcohol or benzene in fine needles or large, pale yellow, somewhat flattened crystals which melt at 108° and belong to the prismatic class of the monoclinic system [$a:b=0.6640:1$; $\beta=70^{\circ}58'$]; sp. gr. 1.522 at 14°.

Methyl 2:4-dinitrophenylmethylcarbamate crystallises from xylene in pale yellow, parallelogramatic plates, which melt at 98° and belong to the prismatic class of the monoclinic system

[$a:b:c=0.7597:1:1.0875$; $\beta=88^{\circ}43\frac{1}{3}'$];

sp. gr. is 1.506 at 14°.

Methyl 2:4:6-trinitrophenylcarbamate melts at 118° and is dimorphous. The α -modification is the one usually separating from solvents and is deposited from acetone in very shiny, colourless or pale yellow crystals belonging to the prismatic class of the monoclinic system [$a:b:c=0.5758:1:0.8382$; $\beta=75^{\circ}41'$]; sp. gr. 1.612 at 19°. The β -modification occasionally separates from alcohol, along with the α -form, in long, orange needles which turn yellow at about 105° and melt somewhat below 118°; these crystals belong to the bipyramidal division of the rhombic system [$a:b=0.6596:1$]; sp. gr. at 19° is 1.601.

Ethyl 2:4-dinitrophenylmethylcarbamate is deposited from a mixture of benzene and light petroleum in large, colourless, shining crystals, which melt at 112° and belong to the prismatic division of the monoclinic system [$a:b:c=0.6525:1:0.7035$; $\beta=69^{\circ}59'$]; sp. gr. 1.461 at 19°.

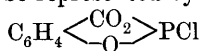
Ethyl 2:4:6-trinitrophenylmethylcarbamate crystallises from a mixture of benzene and light petroleum in slender, transparent, pale yellow needles, which melt at 65° and belong to the prismatic division of the monoclinic system [$a:b:c=0.9759:1:0.3929$; $\beta=67^{\circ}7'$]; sp. gr. at 14°, 1.471.

2:4:6-Trinitrophenylnitromethylamine crystallises from a mixture of benzene and acetone in small, highly refractive, pale yellow needles, which melt at 127° and belong to the prismatic class of the monoclinic system [$a:b:c=2.7823:1:3.5242$; $\beta=75^{\circ}31\frac{1}{2}'$]; sp. gr. at 19°, 1.570.

T. H. P.

Action of Phosphorus Pentachloride and Trichloride on Substituted *o*-Phenolcarboxylic Acids. RICHARD ANSCHÜTZ (*Annalen*, 1906, 346, 286—300. Compare Anschütz and Emery, Abstr., 1887, 946; Anschütz and Moore, Abstr., 1887, 947; Couper,

Compt. rend., 1858, **46**, 1107).—The author discusses the constitution of salicylphosphorous chloride formed by the action of phosphorus trichloride, and of chlorocarboxyphenyl dichloro-orthophosphate formed by the action of phosphorus pentachloride on salicylic acid, and concludes that they must be represented by the formulæ



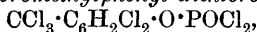
and $\text{COCl} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{POCl}_2$ respectively.

Chlorocarboxyphenyl dichloro-orthophosphate, prepared by the action of phosphorus pentachloride on salicylic acid, is identical with the products of the action of chlorine and of phosphorus pentachloride on salicylphosphorous chloride, as when heated with anhydrous oxalic acid at $75-85^\circ$ all three preparations yield *o*-chlorocarboxyphenyl metaphosphate (Anschütz and Moore, *loc. cit.*), which crystallises from a mixture of benzene and light petroleum, melts at 95° , and boils at $170-171^\circ$ under 11 mm. pressure.

The *additive* compound, formed by the action of bromine on salicylphosphorous chloride, distils at $185-190^\circ$ and is a mixture of the compounds $\text{COBr} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{POClBr}$ and $\text{COCl} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{POBr}_2$, as when heated with anhydrous oxalic acid at $85-100^\circ$ it yields hydrogen chloride and bromide, carbon monoxide and dioxide, and an almost molecular *mixture* of the compounds $\text{C}_7\text{H}_4\text{O}_4\text{ClP}$ and $\text{C}_7\text{H}_4\text{O}_4\text{BrP}$, which melts at $96-98^\circ$ and boils at $205-210^\circ$, or after repeated distillation at $178-182^\circ$ under 11 mm. pressure. G. Y.

Action of Phosphorus Pentachloride and Trichloride on 3:5-Dichlorosalicylic Acid. RICHARD ANSCHÜTZ and HEINRICH MEHRING (*Annalen*, 1906, **346**, 300—311. Compare preceding abstract).—3:5-Dichlorosalicylic acid forms transparent, rhombic crystals [$a:b:c = 0.9983:1:1.2312$] and melts at 219° (214° : Smith, *Abstr.*, 1878, 879). The *chloride*, $\text{OH} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{COCl}$, formed by heating the acid with 1 mol. of phosphorus pentachloride at 60° , crystallises from a mixture of ether and light petroleum, melts at 79° , and is hydrolysed slowly by moist air, quickly by hot water. The methyl ester, which melts at 147° (143° : Smith, *loc. cit.*) and boils at 160° , and the ethyl ester, which forms rhombic crystals [$a:b:c = 0.9403:1:0.4273$], melts at 57° (47° : Smith, *loc. cit.*) and boils at 159° under 11.5 mm. pressure, are prepared by the action of methyl and ethyl alcohols respectively on the acid chloride. The *phenyl ester*, $\text{OH} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{CO}_2\text{Ph}$, crystallises in transparent, rhombic plates [$a:b:c = 0.72877:1:1$], melts at 118.5° , and decomposes at 139° under 14 mm. pressure, forming phenol and poly-3:5-dichlorosalicylide. The *anilide*, $\text{OH} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{CO} \cdot \text{NHPh}$, forms sheaves of transparent crystals, which effloresce when exposed to air, and melts at 134.5° . The *piperidide*, $\text{OH} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{CO} \cdot \text{C}_5\text{H}_{10}\text{N}$, crystallises in asymmetric plates [$a:b:c = 0.6707:1:0.660$] and melts at 108° . The *anhydride*, $\text{O}(\text{CO} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{OH})_2$, formed by boiling the acid chloride with the silver salt suspended in ether, crystallises from chloroform, melts at $186-187^\circ$, and is only sparingly soluble in water. The *silver*, $\text{C}_7\text{H}_3\text{O}_3\text{Cl}_2\text{Ag}$, and *ammonium*, $\text{C}_7\text{H}_7\text{O}_3\text{NCl}_2$, salts were analysed.

4:6-Dichloro-2-trichloromethylphenyl dichloro-orthophosphate,



is prepared by heating 3:5-dichlorosalicylic chloride with 1 mol. of phosphorus pentachloride in a sealed tube at 50—60° for twelve hours; it separates from acetone in transparent crystals, which become opaque on exposure to air, melts at 102—104°, is hydrolysed to 3:5-dichlorosalicylic acid when boiled with water for some hours, and, when heated with 1 mol. of phosphorus pentachloride in a sealed tube at 200° yields a mixture of products boiling at 160—190° under 17 mm. pressure; of these, the main product is probably 2:3:5-trichlorobenzotrichloride.

Poly-3:5-dichlorosalicylide, $(O \cdot C_6H_2Cl_2 \cdot CO)_x$, formed when phenyl 3:5-dichlorosalicylate or 3:5-dichlorosalicylic chloride is distilled under reduced pressure, separates from chloroform in white crystals, becomes blackish-brown at 250°, does not melt at 300°, and remains unaltered when boiled with water.

3:5-Dichlorosalicylphosphorous chloride, $C_6H_2Cl_2 \langle \begin{smallmatrix} CO_2 \\ O \end{smallmatrix} \rangle PCl$, prepared by boiling 3:5-dichlorosalicylic acid with phosphorus trichloride in xylene solution in a reflux apparatus, melts at 55°, boils at 159° under 11 mm. pressure, forms an *additive* compound with chlorine, and is hydrolysed readily by water, forming 3:5-dichlorosalicylic acid.

G. Y.

Action of Phosphorus Pentachloride and Trichloride on 3-Chlorosalicylic Acid. RICHARD ANSCHÜTZ and RICHARD ANSPACH (*Annalen*, 1906, 346, 312—317. Compare preceding abstracts).—3-Chlorosalicylic acid melts at 180° (178°: Varnholt, Abstr., 1887, 945). 3-Chlorosalicylic chloride, $OH \cdot C_6H_3Cl \cdot COCl$, prepared by boiling the acid with phosphorus pentachloride in light petroleum solution in a reflux apparatus, crystallises in long, white needles, melts at 62—63°, and is readily soluble in ether, glacial acetic acid, benzene, chloroform, and carbon tetrachloride. The methyl ester, prepared by the action of methyl alcohol, melts at 38° (83°: Varnholt, *loc. cit.*); the *ethyl ester*, $OH \cdot C_6H_3Cl \cdot CO_2Et$, crystallises from alcohol in long, flat needles and melts at 21°, forming a strongly refractive oil with an aromatic odour, which boils at 147° under 12 mm. or at 269—270° under the ordinary pressure. The *anilide*, $OH \cdot C_6H_3Cl \cdot CO \cdot NHPh$, crystallises from alcohol in white, silvery needles and melts at 158.5—159°.

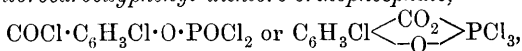
3-Chlorosalicylide and poly-3-chlorosalicylide are formed together with hydrogen chloride when 3-chlorosalicylic chloride is heated about 100° under greatly reduced pressure.

3-Chlorosalicylide, $C_6H_3Cl \langle \begin{smallmatrix} CO \cdot O \cdot C_6H_3Cl \cdot CO \cdot O \\ O \cdot CO \cdot C_6H_3Cl \cdot O \cdot CO \end{smallmatrix} \rangle C_6H_3Cl$? (compare Anschütz, Abstr., 1893, i, 165), is obtained as a white, voluminous powder, melts at 206°, and is readily soluble in chloroform.

Poly-3-chlorosalicylide, $(C_7H_3O_2Cl)_x$, separates from xylene as a hard crust, melts at about 330°, and is insoluble in chloroform.

3-Chlorosalicylphosphorous chloride, $C_6H_3Cl \langle \begin{smallmatrix} CO_2 \\ O \end{smallmatrix} \rangle PCl$, prepared by heating 3-chlorosalicylic acid with phosphorus trichloride in a reflux apparatus, melts at about 65°, boils at 150° under 12.5 mm.

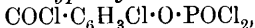
pressure, and when heated with phosphorus pentachloride yields 6-chloro-2-chlorocarboxyphenyl dichloro-orthophosphate,



which boils at 195—196° under 13 mm. pressure and is readily hydrolysed by water. G. Y.

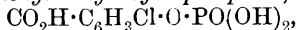
Action of Phosphorus Pentachloride and Trichloride on 5-Chlorosalicylic Acid. RICHARD ANSCHÜTZ and RICHARD ANSPACH (*Annalen*, 1906, **346**, 318—323. Compare preceding abstracts).—

5-Chlorosalicylphosphorous chloride, $\text{C}_6\text{H}_3\text{Cl} \left\langle \begin{array}{c} \text{CO}_2 \\ \text{---O---} \end{array} \right\rangle \text{PCl}$, formed by the action of phosphorus trichloride on 5-chlorosalicylic acid, melts at 55—57°, boils at 155—156° under 14 mm. pressure, is very sensitive to water, and when treated with phosphorus pentachloride at 105—115° yields 4-chloro-2-chlorocarboxyphenyl dichloro-orthophosphate,



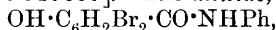
which is formed also by the action of phosphorus pentachloride on 5-chlorosalicylic acid in light petroleum solution. It is obtained as a colourless, strongly refracting oil, which boils at 183—184° under 13 mm. pressure and is easily hydrolysed by moisture.

4-Chloro-2-carboxyphenyl dihydrogen phosphate,



is formed by the action of water on the preceding substance in ethereal solution as a snow-white powder which melts at 161—162°, is hydrolysed to 5-chlorosalicylic acid when boiled with water, and when heated with 1 mol. of phosphorus pentachloride in a sealed tube at 185—190° yields 4-chloro-2-trichloromethylphenyl dichloro-orthophosphate, $\text{CCl}_3 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{O} \cdot \text{POCl}_2$. This melts at 59—60°, boils at 197° under 15 mm. pressure, and when heated with 1 mol. of phosphorus pentachloride in a sealed tube at 210—220° forms 2:5-dichlorobenzo-trichloride, $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{CCl}_3$, which boils at 150° under 13 mm. pressure, and on prolonged boiling with water in a reflux apparatus is hydrolysed, forming 2:5-dichlorobenzoic acid. G. Y.

Action of Phosphorus Pentachloride and Trichloride on 3:5-Dibromosalicylic Acid. RICHARD ANSCHÜTZ and ALFRED ROBITSEK (*Annalen*, 1906, **346**, 323—329. Compare preceding abstracts).—3:5-Dibromosalicylic chloride, $\text{OH} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{COCl}$, prepared by heating 3:5-dibromosalicylic acid with phosphorus pentachloride in light petroleum solution or in a sealed tube at 100°, forms hard, yellow, crystalline aggregates, melts at 86.5°, and when boiled with water yields 3:5-dibromosalicylic acid. The ethyl ester prepared by the action of alcohol on the acid chloride is identical with Freer's ester (Abstr., 1893, i, 66); it crystallises in glistening, rhombic plates [$a:b:c = 0.928715:1:0.519089$]. The anilide,



crystallises from alcohol in glistening needles and melts at 139—140°.

4:6-Dibromo-2-trichloromethylphenyl dichloro-orthophosphate,



formed by heating 3:5-dibromosalicylic acid with 2 mols., or the acid

chloride with 1 mol., of phosphorus pentachloride in a sealed tube at 100°, crystallises in large, colourless plates and melts at 129—130°.

3:5-Dibromosalicylide, $(C_7H_2O_2Br_2)_4$, is prepared by slowly heating 3:5-dibromosalicylic chloride above its melting point under 12 mm. pressure; it separates from a mixture of chloroform and alcohol as a white, flocculent mass, becomes vitreous at 220°, melts at 230°, and when slowly heated resolidifies at 245—260°, forming a *poly*-3:5-dibromosalicylide, $(C_7H_2O_2Br_2)_x$, which is obtained as a white powder, melts and decomposes above 285°, is only sparingly soluble in xylene, is insoluble in other organic solvents or aqueous alkali hydroxides, and is not identical with the *isomerisation product* formed slowly from dibromosalicylide at the ordinary temperature.

3:5-Dibromosalicylphosphorous chloride, $C_6H_2Br_2\begin{smallmatrix} <CO_2> \\ O \end{smallmatrix}PCl$, melts at 75—76°, boils at 210° under 12 mm. pressure, forms an *additive* compound with chlorine, fumes in contact with air, and reacts violently with water, being hydrolysed to 3:5-dibromosalicylic acid.

G. Y.

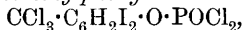
Action of Phosphorus Pentachloride and Trichloride on 3:5-Di-iodosalicylic Acid. RICHARD ANSCHÜTZ, ALFRED ROBITSEK, and FRITZ SCHMITZ (*Annalen*, 1906, **346**, 330—335. Compare preceding abstracts).—3:5-Di-iodosalicylic chloride, $OH \cdot C_6H_2I_2 \cdot COCl$, is prepared by heating 3:5-di-iodosalicylic acid with 1 mol. of phosphorus pentachloride in benzene solution at 60°; it forms yellow, crystalline, nodular aggregates, melts at 97—98°, does not react with phosphorus oxychloride at 100°, and is hydrolysed rapidly when heated with water.

The *methyl ester*, $OH \cdot C_6H_2I_2 \cdot CO_2Me$, formed by the action of methyl alcohol on the acid chloride, melts at 110° and boils and decomposes partially at 221° under 17 mm. pressure. The *ethyl ester*, $C_9H_8O_3I_2$, crystallises in glistening, rhombic leaflets, melts at 133°, and decomposes above 200° when heated under reduced pressure. The *anilide*, $OH \cdot C_6H_2I_2 \cdot CO \cdot NHPh$, melts and decomposes at 173.5°.

When heated above its melting point under 15 mm. pressure, 3:5-di-iodosalicylic chloride forms two di-iodosalicylides. α -3:5-Di-iodosalicylide, $(C_7H_2O_2I_2)_x$, separates from a mixture of chloroform and alcohol as a white, flocculent mass, becomes vitreous at 120°, melts at about 145°, is readily soluble in chloroform or xylene, and decomposes liberating iodine when exposed to light.

β -3:5-Di-iodosalicylide, $(C_7H_2O_2I_2)_x$, formed chiefly at 150°, crystallises from xylene as a white crust, melts at 101°, and is insoluble in chloroform.

4:6-Di-iodo-2-trichloromethylphenyl dichloro-orthophosphate,



prepared by heating 3:5-di-iodosalicylic acid with 2 mols. of phosphorus pentachloride in a sealed tube at 100° for ten hours, crystallises from light petroleum in large, stellate aggregates, melts at 126°, and is hydrolysed to 3:5-di-iodosalicylic acid when boiled with water.

3:5-Di-iodosalicylphosphorous chloride, $C_6H_2I_2\begin{smallmatrix} <CO_2> \\ O \end{smallmatrix}PCl$, formed by heating 3:5-di-iodosalicylic acid with an excess of phosphorus

trichloride, melts at 126° , decomposes when heated under reduced pressure, and is hydrolysed readily by water. G. Y.

Action of Phosphorus Pentachloride and Trichloride on Nitro- and Halogen-nitro-salicylic Acids. RICHARD ANSCHÜTZ, EVERHARD WEBER, JULIUS SIEBEN, and RICHARD ANSPACH (*Annalen*, 1906, **346**, 336—340. Compare preceding abstracts).—3:5-Dinitro-salicylic chloride, $\text{OH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{COCl}$, is prepared by the action of phosphorus pentachloride on 3:5-dinitrosalicylic acid in light petroleum solution; it crystallises from a mixture of benzene and light petroleum in small, thin needles, melts at $69\text{--}70^{\circ}$, and reacts with methyl and ethyl alcohols, forming the esters which melt at 125° and 98° respectively (Cahours, *Annalen*, 1849, **69**, 230, 235), and are formed also by the action of methyl and ethyl alcohols on the products of the reaction of the acid chloride with methyl and ethyl sodiomalonates. When heated to $70\text{--}80^{\circ}$, the acid chloride evolves hydrogen chloride and yields an impure 3:5-dinitrosalicylide, $(\text{C}_7\text{H}_2\text{O}_6\text{N}_2)_x$, which is obtained as a greyish-yellow powder, melts at $150\text{--}155^{\circ}$, is hydrolysed by cold water forming 3:5-dinitrosalicylic acid, and when treated with ethyl alcohol in chloroform solution forms ethyl 3:5-dinitrosalicylate.

3-Nitrosalicylic chloride, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{COCl}$, formed in the same manner as the 3:5-dinitro-acid chloride, crystallises from a mixture of benzene and light petroleum in sheaves of large, long plates, melts at $59\text{--}61^{\circ}$, and is hydrolysed to 3-nitrosalicylic acid when boiled with water.

5-Chloro-3-nitrosalicylic chloride, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)\cdot\text{COCl}$, formed from 5-chloro-3-nitrosalicylic acid melting at 163° , could not be purified from phosphorus pentachloride; when treated with alcohol, it yields the ethyl ester, melting at $90\text{--}91^{\circ}$.

5-Bromo-3-nitrosalicylic chloride, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)\cdot\text{COCl}$, separates from a mixture of benzene and light petroleum in stout, yellow crystals and melts at $56\cdot5^{\circ}$.

3-Bromo-5-nitrosalicylic chloride, $\text{C}_7\text{H}_3\text{O}_4\text{NClBr}$, forms stout, white crystals and melts at $95\text{--}96^{\circ}$. G. Y.

Action of Phosphorus Pentachloride and Trichloride on β -Cresotic Acid [2-Hydroxy-*m*-toluic Acid; 3-Methylsalicylic Acid]. RICHARD ANSCHÜTZ, ERNST SCHROEDER, EVERHARD WEBER, and RICHARD ANSPACH (*Annalen*, 1906, **346**, 341—349. Compare preceding abstracts).—2-Hydroxy-*m*-toluoyl chloride, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{COCl}$, prepared by the action of phosphorus pentachloride on 2-hydroxy-*m*-toluic acid in light petroleum solution, solidifies in a freezing mixture and melts at $27\text{--}28^{\circ}$. Silver 2-hydroxy-*m*-toluate, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}_2\text{Ag}$, forms a white, granular powder, which blackens slowly on exposure to light. The amide, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{NH}_2$, crystallises from dilute alcohol in small, dull, white needles and melts at 112° ; the anilide, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{NHPh}$, crystallises in sheaves of needles and melts at 123° ; the piperidide, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{C}_5\text{H}_{10}\text{N}$, forms monoclinic plates [$a:b:c = 1\cdot34217:1:1\cdot88072$; $\beta = 77^{\circ}29\cdot5'$] and melts at 53° .

3-Methylsalicylphosphorous chloride, $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{CO}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{PCl}$, prepared by boiling 2-hydroxy-*m*-toluic acid with phosphorus trichloride in xylene solution in a reflux apparatus, melts at $36\text{--}37^\circ$, boils at $143.6\text{--}144^\circ$ under 14 mm. pressure, and when heated with phosphorus pentachloride forms 3-chlorocarboxy-*o*-tolyl dichloro-orthophosphate, $\text{COCl} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{O} \cdot \text{POCl}_2$, which is formed also by the action of chlorine on the fused phosphorous chloride. It is obtained as a transparent liquid, which boils at $185.6\text{--}186.2^\circ$ under 12 mm. pressure and is hydrolysed by moisture.

3-Methylsalicylphosphoric chloride dibromide, $\text{COBr} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{O} \cdot \text{POClBr}$ or $\text{COCl} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{O} \cdot \text{POBr}_2$, prepared by the action of bromine on the phosphorous chloride, is obtained as a transparent oil which boils at $200\text{--}202^\circ$ under 15 mm. pressure, is very unstable, and forms 2-hydroxy-*m*-toluic acid when boiled with aqueous sodium hydroxide.

3-Trichloromethyl-*o*-tolyl dichloro-orthophosphate, $\text{CCl}_3 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{O} \cdot \text{POCl}_2$, prepared by boiling 2-hydroxy-*m*-toluic acid with 2 mols. of phosphorus pentachloride in carbon tetrachloride solution in a reflux apparatus, crystallises in prismatic plates, melts at 80° , boils at $199.4\text{--}199.8^\circ$ under 13 mm. pressure, and is hydrolysed readily by water in ethereal solution, forming 3-carboxytolyl dihydrogen phosphate, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{O} \cdot \text{PO}(\text{OH})_2$; this is a white, crystalline substance and melts at $148\text{--}149^\circ$.

G. Y.

Action of Phosphorus Pentachloride and Trichloride on *m*-Cresotic Acid (3-Hydroxy-*p*-toluic Acid; 4-Methylsalicylic Acid). RICHARD ANSCHÜTZ and ERNST SCHROEDER (*Annalen*, 1906, 346, 349—353. Compare preceding abstracts).—4-Chlorocarboxy-3-tolyl dichloro-orthophosphate, $\text{COCl} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{O} \cdot \text{POCl}_2$, formed by the action of phosphorus pentachloride on 3-hydroxy-*p*-toluic acid or by the action of chlorine or phosphorus pentachloride on 4-methylsalicylphosphorous chloride, is obtained as a clear, strongly refracting, viscid liquid, which boils at $184.6\text{--}185.4^\circ$ under 12 mm. pressure, and, when heated with phosphorus pentachloride in a sealed tube at $165\text{--}170^\circ$, yields 4-trichloromethyl-3-tolyl dichloro-orthophosphate,



this could not be purified from accompanying substitution products.

4-Chlorocarboxy-3-tolyl metaphosphate, $\text{COCl} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{O} \cdot \text{PO}_2$, prepared by carefully heating the dichloro-orthophosphate with anhydrous oxalic acid and distilling the product under reduced pressure, crystallises in long plates, melts at about 77° , and boils at $195.4\text{--}196.2^\circ$ under 14 mm. pressure.

4-Carboxy-3-tolyl dihydrogen phosphate, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{O} \cdot \text{PO}(\text{OH})_2$, formed by the action of water on the dichloro-orthophosphate, melts at 150° .

4-Methylsalicylphosphorous chloride, $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{CO}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{PCl}$, prepared by heating 3-hydroxy-*p*-toluic acid with phosphorus trichloride in xylene

solution in a reflux apparatus, forms a white, crystalline mass, melts at 45° , and boils at $150\text{--}151^{\circ}$ under 13 mm. pressure.

4-Methylsalicylphosphoric chloride dibromide, $\text{COCl}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\cdot\text{POBr}_2$ or $\text{COBr}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\cdot\text{POClBr}$, prepared by the action of bromine on 4-methylsalicylphosphorous chloride, is obtained as a clear, viscid liquid, which soon becomes yellow, boils at $202\text{--}203^{\circ}$ under 13 mm. pressure, and is readily hydrolysed by moisture. G. Y.

Action of Phosphorus Pentachloride and Trichloride on *p*-Cresotic Acid (5-Methylsalicylic Acid; 4-Hydroxy-*m*-toluic Acid). RICHARD ANSCHÜTZ and ERNST SCHROEDER (*Annalen*, 1906, 346, 354—357. Compare preceding abstracts).—**2-Chlorocarboxy-*p*-tolyl dichloro-orthophosphate**, $\text{COCl}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\cdot\text{POCl}_2$, formed by the action of phosphorus pentachloride on 4-hydroxy-*m*-toluic acid or of phosphorus pentachloride or chlorine on 5-methylsalicylphosphorous chloride, is obtained as a transparent, strongly refracting liquid, which boils at 185° under 12 mm. pressure, yields 4-hydroxy-*m*-toluic acid when boiled with water, and when heated with phosphorus pentachloride in a sealed tube at $165\text{--}170^{\circ}$ forms a mixture of products boiling at $183\text{--}225^{\circ}$ under 13 mm. pressure.

2-Chlorocarboxy-*p*-tolyl metaphosphate, $\text{COCl}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\cdot\text{PO}_2$, formed by the action of anhydrous oxalic acid or the dichloro-orthophosphate, crystallises from ether in plates, melts at 88° , and boils at $185\text{--}186^{\circ}$ under 14 mm. pressure.

2-Carboxy-*p*-tolyl dihydrogen phosphate, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\cdot\text{PO}(\text{OH})_2$, forms a white, crystalline mass and melts at $139\cdot5\text{--}140\cdot4^{\circ}$.

5-Methylsalicylphosphorous chloride, $\text{C}_6\text{H}_3\text{Me}\cdot\text{C}(\text{CO}_2)\text{OPCl}$, melts at 61° , boils at $145\cdot6\text{--}146\cdot4^{\circ}$ under 12 mm. pressure, and reacts with bromine forming 5-methylsalicylphosphoric chloride dibromide,

$\text{COCl}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\cdot\text{POBr}_2$ or $\text{COBr}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\cdot\text{POClBr}$, which solidifies in a freezing mixture and melts in the hand to a transparent oil boiling at $205\text{--}207^{\circ}$ under 15 mm. pressure; it is easily hydrolysed by water. G. Y.

Action of Phosphorus Pentachloride and Trichloride on 2-Hydroxyuvitic Acid. RICHARD ANSCHÜTZ and ALFRED ROBITSEK (*Annalen*, 1906, 346, 357—360. Compare preceding abstracts).—**2-Hydroxyuvityl dichloride**, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Me}(\text{COCl})_2$ [$\text{OH}:\text{Me}:\text{COCl}:\text{COCl}=2:3:1:5$], prepared by the action of phosphorus pentachloride on 2-hydroxyuvitic acid in light petroleum solution, crystallises in sheaves of colourless needles, melts at $67\text{--}68^{\circ}$, decomposes when distilled under reduced pressure, is moderately stable when exposed to air, and is hydrolysed when heated with water. The dimethyl ester, formed by the action of methyl alcohol on the dichloride, melts at 132° (128° : Jacobsen, *Abstr.*, 1881, 431); the diethyl ester, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Me}(\text{CO}_2\text{Et})_2$, crystallises from light petroleum in colourless needles and melts at 62° . The dianilide, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Me}(\text{CO}\cdot\text{NHPh})_2$, crystallises in transparent prisms which soon become opaque and melts at 238° .

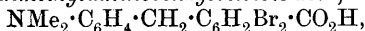
The action of phosphorus trichloride on 2-hydroxyuvitic acid leads to the formation of an extremely hygroscopic, colourless, viscid oil, which reacts energetically with water, forming 2-hydroxyuvitic acid. G. Y.

Action of Phosphorus Pentachloride on 1-Hydroxy-2-Naphthoic Acid. RICHARD ANSCHÜTZ, EVERHARD WEBER, and KARL RUNKEL (*Annalen*, 1906, **346**, 360—381. Compare preceding abstracts; Wolfenstein, *Abstr.*, 1887, 963; 1888, 714).—After purification by conversion into the ammonium salt and precipitation by hydrochloric acid, 1-hydroxy-2-naphthoic acid melts at 191—192° (187°: Schmidt and Burkhardt, *Abstr.*, 1888, 59). 1-Hydroxy-2-naphthoyl chloride, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{COCl}$, formed by the action of phosphorus pentachloride on the acid in light petroleum solution, crystallises in long, yellow needles, melts at 85—86°, and when treated with ammonia in ethereal solution yields the *amide* $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}\cdot\text{NH}_2$, which forms yellow, granular crystals and melts at 202°. The *anilide*, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}\cdot\text{NHPh}$, forms white, glistening crystals and melts at 154°.

The chief part of this paper consists of a *résumé* and discussion of the results described in this and the preceding papers. G. Y.

3 : 6-Dibromo-2'-dimethylaminobenzoylbenzoic Acid, the Corresponding Diethyl Compound, and their Derivatives. ÉMILE SÉVERIN (*Compt. rend.*, 1906, **142**, 1274—1276. Compare *Abstr.*, 1900, i, 296, 450, 598).—3 : 6-Dibromo-2'-dimethylaminobenzoylbenzoic acid, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CO}_2\text{H}$, prepared by Haller and Guyot's method (compare *Abstr.*, 1894, i, 602) from 1 : 4-dibromophthalic acid (Guareschi, *Abstr.*, 1888, 1300), crystallises from alcohol in magnificent citron-yellow plates and melts at 249°; the *acetate* (mixed anhydride) crystallises from benzene and alcohol in brilliant plates and melts at 195°; the *methyl* ester prepared by the action of sodium methoxide on the acetate forms white, highly refractive crystals which melt at 180°; the *ethyl* ester, similarly prepared, melts at 173°; the *nitroso*-derivative $\text{NO}\cdot\text{NMe}_2\cdot\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CO}_2\text{H}$, prepared by the action of sodium nitrite on the original acid, forms pale yellow needles which melt at 165°.

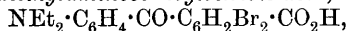
3 : 6-Dibromo-2'-dimethylaminobenzoylbenzoic acid,



obtained by reducing the corresponding benzoylbenzoic acid, crystallises with difficulty, melts at 253°, and is converted into 1-dimethylamino-

5 : 8-dibromoanthraquinone, $\text{C}_6\text{H}_2\text{Br}_2\cdot\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}\cdot\text{C}_6\text{H}_3\cdot\text{NMe}_2$, by the prolonged action of concentrated sulphuric acid at 66°; this compound forms bronze-red needles and melts at 218°.

3 : 6-Dibromo-2'-diethylaminobenzoylbenzoic acid,



forms yellow plates and melts at 221°; the *acetate* forms white plates and melts at 159°, and the *methyl* ester forms refractive crystals and melts at 186°.

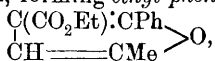
M. A. W.

Formation of Unsaturated Ketolactones from $\alpha\beta$ Diacylcarboxylic Esters. WALTHER BORSCHKE and ALBERT FELS (*Ber.*, 1906, **39**, 1809—1818).—Ethyl acetophenoneacetoacetate (Paal, *Abstr.*, 1883, 598) is quantitatively obtained from ethyl sodioacetoacetate and ω -bromoacetophenone in ethereal solution. When heated with sodium ethoxide, or when distilled, the ester yields Paal's dehydroacetophenone-acetone-

carboxylic acid (Abstr., 1885, 248), which, from its general behaviour and from its resemblance to Knorr's acetylangelicalactone (Abstr., 1899, i, 194; compare also Abstr., 1889, 384; 1897, i, 63), the author concludes to be the lactone of γ -hydroxy- α -acetyl- γ -phenyl- Δ^{β} -butenoic acid, $\begin{array}{c} \text{CHAc}\cdot\text{CO} \\ | \\ \text{CH}=\text{CPh} \end{array} > \text{O}$. It reduces ammoniacal silver solutions, is soluble

in alkali carbonates, develops a greenish-blue coloration with ferric chloride, and is reconverted into the parent substance by boiling alcohol. By benzylation in pyridine, a *benzoate* is obtained, which separates from alcohol in long, rose-red needles, melts at $160-161^{\circ}$, and is converted by phenylhydrazine in alcoholic solution into the *phenylhydrazone* of the original lactone, which crystallises in golden-yellow needles and melts at 168° . The *semicarbazone* melts and decomposes at 264° . C. S.

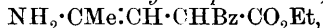
Synthetical Experiments with Ethyl Benzoylacetonylacetate. WALTHER BORSCHKE and ALBERT FELS (*Ber.*, 1906, 39, 1922—1929).—Ethyl benzoylacetonylacetate, $\text{CH}_2\text{Ac}\cdot\text{CHBz}\cdot\text{CO}_2\text{Et}$, is prepared by heating ethyl sodiobenzoylacetate with iodoacetone in alcoholic solution; it is obtained as a dark-coloured, heavy oil, which decomposes when distilled, forming *ethyl phenuvate*,



which distils at $193-194^{\circ}$ under 20 mm. pressure, and on hydrolysis yields phenuvic acid (compare Paal, *Habilitations-schrift*, Wurzburg, 1890). On elimination of carbon dioxide, this acid yields 2-phenyl-5-methylfuran.

1-Phenyl- Δ^1 -cyclopentene-3-one, $\begin{array}{c} \text{CH}_2\cdot\text{CPh} \\ | \\ \text{CH}_2-\text{CO} \end{array} > \text{CH}$ is formed together with benzoic and lævulic acids when ethyl benzoylacetonylacetate is boiled with 2 per cent. aqueous sodium hydroxide; it is identical with Paal's dehydrophenacylacetone (Abstr., 1884, 1177). The action of 2 per cent. alcoholic potassium hydroxide on ethyl benzoylacetonylacetate at the ordinary temperature leads to the formation of phenacylacetone, which is isolated as the 4-phenylsemicarbazone, $\text{C}_{25}\text{H}_{26}\text{O}_2\text{N}_6$, crystallising in white needles and melting at $194-195^{\circ}$. When heated with dilute hydrochloric acid, ethyl benzoylacetonylacetate yields ethyl phenuvate, which is hydrolysed and partially decomposed, yielding 2-phenyl-5-methylfuran, together with a small amount of phenylcyclopentenone.

The action of ammonia on ethyl benzoylacetonylacetate leads to the formation of *ethyl γ -amino- α -benzoyl- Δ^{β} -pentenoate*,

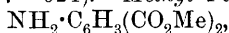


which readily changes into *ethyl 2-phenyl-5-methylpyrrole-3-carboxylate*, $\text{C}_4\text{NH}_2\text{MePh}\cdot\text{CO}_2\text{Et}$. The action of aniline on ethyl benzoylacetonylacetate leads to the formation of 1:2-diphenyl-5-methylpyrrole-3-carboxylate, $\text{C}_4\text{NHMePh}_2\cdot\text{CO}_2\text{Et}$, which crystallises in glistening needles and melts at 133.5° . The acid, $\text{C}_{13}\text{H}_{15}\text{O}_2\text{N}$, crystallises in glistening, silvery leaflets and melts and decomposes at 267° , forming carbon dioxide and 1:2-diphenyl-5-methylpyrrole.

Ethyl benzoylacetonylacetate reacts with semicarbazide in alcoholic solution, forming a *product*, $C_{15}H_{17}O_3N_3$, which crystallises in white needles, melts at $224-226^\circ$, and is readily soluble in hot alcohol, together with a small quantity of the sparingly soluble *semicarbazone* of the ketone, $C_{14}H_{16}O_3 \cdot N \cdot NH \cdot CO \cdot NH_2$, which melts at $255-260^\circ$.

The *product*, $C_{26}H_{28}O_2N_4$, of the condensation of ethyl benzoylacetonylacetate with phenylhydrazine crystallises in glistening needles and melts and decomposes at $139-140^\circ$. G. Y.

Methyl 4-Aminophthalate and Certain of its Acyl Derivatives. MARSTON T. BOGERT and ROEMER R. RENSHAW (*J. Amer. Chem. Soc.*, 1906, 28, 617—624).—*Methyl 4-aminophthalate*,



obtained by the reduction of methyl 4-nitrophthalate, crystallises in alcohol or benzene in white, lustrous plates, and from water in long, hexagonal prisms, melts at 84° (corr.), and is soluble in alcohol, acetone, or chloroform, and slightly so in hot water, carbon tetrachloride, or ether. The *hydrochloride* forms a crystalline mass.

By the action of glacial formic acid on the ester, the *compound*, $C_6H_3(CO_2Me)_2 \cdot NH \cdot CH \cdot N \cdot C_6H_3(CO_2Me)_2$, is obtained, which forms nearly colourless, microscopic crystals, melts at 179° (corr.), and is soluble in alcohol, hot ethyl acetate, acetone, or benzene. *Methyl 4-acetylaminophthalate*, $NHAc \cdot C_6H_3(CO_2Me)_2$, obtained by the action of acetic anhydride on the ester, crystallises in small, colourless plates and melts at 136.5° (corr.). The corresponding *propionyl* derivative crystallises in long, thin, colourless needles and melts at 110.5° (corr.). The *isobutyryl* derivative forms long, thin, colourless needles and melts at $122-123^\circ$ (corr.). The *benzoyl* derivative forms colourless needles and melts at $132-132.5^\circ$ (corr.). The *m-nitrobenzoyl* derivative crystallises in nearly colourless scales and melts at 147° (corr.). The *p-nitrobenzoyl* derivative crystallises from alcohol in small, yellow flakes and melts at 202° (corr.).

Methyl 4-urethanophthalate, $C_6H_3(CO_2Me)_2 \cdot NH \cdot CO_2Et$, separates from boiling water in long needles and melts at 122° (corr.). *Methyl 4-phenyluraminophthalate*, $C_6H_3(CO_2Me)_2 \cdot NH \cdot CO \cdot NHPh$, forms microscopic needles and melts at 138° (corr.).

Methyl 4-ethyloxalylaminophthalate, $C_6H_3(CO_2Me)_2 \cdot NH \cdot CO \cdot CO_2Et$, obtained by the action of ethyl oxalate on the ester, crystallises in small, white flakes and melts at 121.5° (corr.). *Methyl oxalyl-4-aminophthalate*, $C_2O_2[NH \cdot C_6H_3(CO_2Me)_2]_2$, obtained as a white precipitate in the preparation of the preceding compound, melts at 239° (corr.). The *phthalamic acid*, $C_6H_3(CO_2Me)_2 \cdot NH \cdot CO \cdot C_6H_4 \cdot CO_2H$, forms microscopic crystals and melts at $166-167^\circ$ (corr.); its *silver* salt is described. The corresponding *succinamic acid* crystallises from water in colourless needles, melts at 173° (corr.), and loses water with probable formation of the imide; the *silver* salt is described. 4-*Aminophthalanil*, $NH_2 \cdot C_6H_3 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} NPh$, obtained by boiling methyl 4-aminophthalate with aniline, crystallises in long, yellow needles and melts at 205.5° (corr.). E. G.

Synthesis of Ethyl Tetrahydroquinonedicarboxylate.
 HYPOLYT TREPHILIEFF (*Ber.*, 1906, **39**, 1863—1864).—When ethyl sodioacetoacetate (1 mol.) and ethyl γ -bromoacetoacetate react in ethereal solution, a yellow, crystalline substance is obtained, which is Duisberg's ethyl tetrahydroquinonedicarboxylate (*Abstr.*, 1882, 1192).
 C. S.

Benzaldehyde Derivatives of Sugars and Glucosides.
 WILLIAM ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Rec. trav. chim.*, 1906, **25**, 153—161. Compare Lobry de Bruyn and Alberda van Ekenstein, *Abstr.*, 1899, i, 661; 1900, i, 619; 1902, i, 745; and Schiff, *Abstr.*, 1888, 572).—These products are obtained usually by mixing the sugar with benzaldehyde and adding phosphoric oxide gradually with constant stirring. The mixture is set aside for some time and then poured into water, when the condensation product separates usually as a crystalline powder, which is recrystallised from hot methyl alcohol or from chloroform. None of the products reduce Fehling's solution, and all are hydrolysed into their generators by boiling with dilute sulphuric acid.

Dibenzylidenearabinose, $C_7H_6 \begin{array}{c} \diagup O \cdot CH \cdot O \cdot CH \cdot CH_2 \cdot O \\ \diagdown O \cdot CH \cdot CH \cdot O \cdot C_7H_6 \end{array}$, melts at 154° , has $[\alpha]_D + 26.8^\circ$ in methyl alcohol (showing no mutarotation), and is not acted upon by emulsin at 35° . The number of benzylidene groups present may be determined by boiling a solution of the substance with phenylhydrazine and dilute sulphuric acid and weighing the benzaldehydephenylhydrazone formed.

Dibenzylidenexylose melts at 130° , has $[\alpha]_D + 37.5^\circ$. *Dibenzylidenexylo-rhamnose* melts at 128° , has $[\alpha]_D + 56.3^\circ$, and is hydrolysed with difficulty by dilute sulphuric acid.

Amorphous *dibenzylidene* derivatives of dextrose, mannose, galactose, lævulose, and sorbose were obtained, possibly mixed with monobenzylidene derivatives. The crude products react with acetic anhydride, forming *monoacetyl* derivatives. Glucosides condense readily with benzaldehyde when heated with it in presence of anhydrous sodium sulphate. The products do not reduce Fehling's solution, and are hydrolysed by boiling with dilute sulphuric acid.

Benzylidene- α -methylglucoside crystallises from boiling water, melts at 158° , and has $[\alpha]_D + 85^\circ$ in aqueous solution. *Benzylidene- β -methylglucoside* melts at 194° , has $[\alpha]_D - 75^\circ$ in methyl alcohol, and is not acted on by emulsin. α -Methylmannoside gives rise to both a *mono-* and a *di-benzylidene* derivative. The first melts at 110° , is slightly lævorotatory, and readily soluble in water; the second melts at 178° and has $[\alpha]_D - 5^\circ$ in chloroform. *Benzylidene- α -methylgalactoside* melts at 152° and has $[\alpha]_D + 120.7^\circ$ in methyl alcohol.

Benzylidenesalicin crystallises from methyl alcohol, melts at 187° , and has $[\alpha]_D - 48.3^\circ$ in acetone. *Benzylidenearbutin* melts at 218° and has $[\alpha]_D - 24.2^\circ$ in methyl alcohol.

Di-p-toluyldidenearabinose, produced by condensation in presence of phosphoric oxide at the atmospheric temperature, crystallises from methyl alcohol, melts at 164° , and has $[\alpha]_D + 2.9^\circ$ in chloroform. The corresponding *xylose* derivative melts at 140° , has $[\alpha]_D + 45.6^\circ$ in

acetone, and is hydrolysed with difficulty by boiling with dilute sulphuric acid. *p*-Toluylidene- α -methylglucoside melts at 178° and has $[\alpha]_D + 83.2^\circ$ in methyl alcohol. The corresponding derivative of methylmannoside is a syrup, and has $[\alpha]_D + 29.5^\circ$; that of α -methylgalactoside melts at 146° and has $[\alpha]_D + 142^\circ$ in methyl alcohol, and that of salicin melts at 144° and has $[\alpha]_D - 16^\circ$ in methyl alcohol.

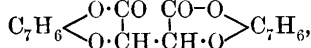
The product formed by condensing β -methylglucoside with cumin-aldehyde in presence of anhydrous sodium sulphate, melts at 124° and has $[\alpha]_D - 34.8^\circ$.

Salicylaldehyde does not condense with sugars in presence of phosphoric oxide, but reacts readily with glucosides. The α -methylglucoside mono-derivative separates from warm water in colourless crystals, melts at 182° and has $[\alpha]_D + 91.2^\circ$ in water. The product formed with salicin melts at 163° and has $[\alpha]_D - 32^\circ$ in methyl alcohol.

T. A. H.

Benzylidene and Toluylidene Derivatives of Hydroxy-acids.

ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Rec. trav. chim.*, 1906, 25, 162—164. Compare Alberda van Ekenstein, 1901, i, 120; Lobry de Bruyn and Alberda van Ekenstein, 1899, i, 904; 1902, i, 76, and preceding abstract).—*Dibenzylidene-d-tartaric acid*,



prepared by condensing benzaldehyde with tartaric acid in presence of phosphoric oxide, crystallises from methyl alcohol in long, colourless needles, melts at 145°, has $[\alpha]_D + 128^\circ$ in methyl alcohol, and is hydrolysed by boiling dilute sulphuric acid. The similar condensation product formed with tolualdehyde crystallises from a mixture of light petroleum and benzene, melts at 177°, and has $[\alpha]_D + 107^\circ$ in methyl alcohol. The *l*-tartaric acid derivative melts at 166° and has $[\alpha]_D - 85.8^\circ$, and that of racemic acid, which may be obtained from racemic acid or by crystallising together the ditoluylidene derivatives of *d*- and *l*-tartaric acids, melts at 152°.

Benzylidenecitric acid, $\text{C}(\text{CH}_2 \cdot \text{CO}_2\text{H})_2 \begin{array}{c} \diagup \text{CO} \cdot \text{O} \\ \diagdown \text{O} - \text{C}_7\text{H}_6 \end{array}$, prepared by the general method, crystallises from a mixture of benzene and light petroleum and melts at 178°. The potassium and sodium salts are amorphous; those of barium and calcium are slightly soluble in water. Saccharic, isosaccharic, and gulonic acids also condense with benzaldehyde in presence of phosphoric oxide.

T. A. H.

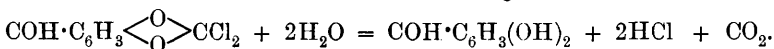
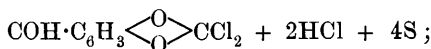
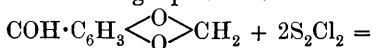
Sulphonation of 2-Chloro-5-nitrobenzaldehyde with Alkali Sulphites. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 165613).—On boiling 2-chloro-5-nitrobenzaldehyde with aqueous alkali sulphites, sulphonation does occur, but the product is contaminated with a large amount of diazotisable substances. A quantitative yield of 5-nitrobenzaldehyde-2-sulphonic acid is obtained, however, on heating an alcoholic solution of the foregoing aldehyde with sodium sulphite, which remains in suspension in this medium. From the alcoholic filtrate, the sodium salt of the sulphonic acid separates on cooling in yellow crystals.

G. T. M.

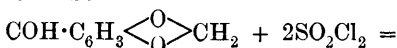
Preparation of Protocatechualdehyde. FRANZ FRITZSCHE & Co. (D.R.-P. 162822).—Heliotropin is converted almost quantitatively into protocatechualdehyde by heating at 185—190° under 12 atmospheres pressure with dilute acids or acid metallic salts. The charring which is observed when heliotropin is heated alone at 200° does not take place.

C. H. D.

Preparation of Protocatechuic Aldehyde from Piperonaldehyde or its Chloride. SCHIMMEL & Co. (D.R.-P. 165727).—Piperonaldehyde may be converted directly into protocatechuic aldehyde by heating at 130° with sulphur chloride (S_2Cl_2) until the evolution of hydrogen chloride has ceased, then boiling with water, filtering the solution from precipitated sulphur, and extracting the required aldehyde with ether. The reactions involved may be expressed by the following equations:



This change may also be effected either with sulphur dichloride (SCl_2) or by passing chlorine into a mixture of sulphur and piperonaldehyde. The chlorination stage of the process may also be effected with sulphuryl chloride, in which case the action takes place as follows:



G. T. M.

2-Chlorocyclohexanone and its Derivatives. LOUIS BOUVEAULT and F. CHEREAU (*Compt. rend.*, 1906, 142, 1086—1087).—2-Chlorocyclohexanone is obtained by treating cyclohexanone or cyclohexanol in water with chlorine in presence of calcium carbonate. When freshly prepared it is a colourless liquid and boils at 82—83°, but gradually solidifies, forming splendid crystals, and melts at 23°. When boiled with a strong solution of potassium carbonate in water, it passes into 2-hydroxycyclohexanone. This sublimes at 25° under reduced pressure and at 100° under atmospheric pressure, melts at 113° in a closed tube, and is very soluble in warm alcohol, less so in cold, and insoluble in ether or light petroleum. The semicarbazone is colourless and melts at 165°. On oxidation with permanganate, it furnishes adipic acid. Nitric acid converts it into oxalic and succinic acids.

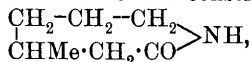
1-Methyl-6-cyclohexanone, prepared from 2-chlorocyclohexanone by the Grignard reaction, boils at 160° under 10 mm. pressure; the semicarbazone melts at 195°. 1-Ethyl-6-cyclohexanone boils at 65° under 10 mm. pressure: its semicarbazone melts at 157°. 1-isoPropyl-6-cyclohexanone boils at 80° under 10 mm. pressure.

T. A. H.

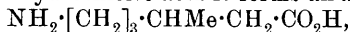
Terpenes and Etheral Oils. LXXIX. Compounds of the cyclo-Hexanone Series. OTTO WALLACH (*Annalen*, 1906, **346**, 249—265. Compare Sabatier and Mailhe, *Abstr.*, 1905, i, 275).—The properties of 1:2-, 1:4-, and 1:3-methylcyclohexanones are compared. Under the conditions described previously (*Abstr.*, 1900, i, 590), the oxime of 1:2-methylcyclohexanone is converted into the isooxime, which crystallises in prisms or needles, melts at 90—91°, and forms an insoluble *hydrochloride*, $C_{17}H_{13}ON, HCl$.

1:4-Methylcyclohexanone, prepared by Sabatier and Mailhe's method (*loc. cit.*), boils at 169—171°; it forms a characteristic, yellow *dibenzylidene* derivative, $CHMe \begin{smallmatrix} \text{CH}_2 \cdot C(CHPh) \\ \text{CH}_2 \cdot C(CHPh) \end{smallmatrix} > CO$, melting at 98—99°, and an *oxime* melting at 37—39° and boiling at about 114° under 14 mm. pressure. The corresponding isooxime, which is very soluble, yields a solid *hydrochloride*, $C_7H_{13}ON, HCl$.

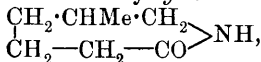
α -isooxime of 1:3-methylcyclohexanone (*Abstr.*, 1900, i, 590), melting at 104—105°, must have the constitution



as when boiled with hydrochloric acid it forms an *amino-acid*,



which, on oxidation with alkaline permanganate, yields β -methyladipic acid. The β -isooxime of 1:3-methylcyclohexanone,



when boiled with hydrochloric acid, yields the *hydrochloride* of the amino-acid, $CO_2H \cdot [CH_2]_3 \cdot CHMe \cdot CH_2 \cdot NH_2, HCl$, which, when treated with sodium nitrite and oxidised with chromic acid, forms γ -acetylbutyric acid; the semicarbazone of this melts at 177° (compare *Abstr.*, 1904, i, 752).

The oxime of 3:5:5-trimethylcyclohexanone (*Abstr.*, 1902, i, 806) melts at 84—85° (58°: Knoevenagel and Fischer, *Abstr.*, 1897, i, 611); it yields two isooximes: the α -isooxime crystallises in prisms and melts at 111—112°; the more soluble β -isooxime melts at 82—84°.

In addition to the α -isooxime melting at 115—116° (*Abstr.*, 1902, i, 805), a more soluble β -isooxime, melting at 106—108°, has been obtained from the oxime of 2:4:4-trimethylcyclohexanone.

[With KARL HÜTTNER and JOHANNES ATTENBURG.]—The base boiling at 273°, obtained by treating 1:3-methylcyclohexanone with ammonium formate (this vol., i, 160; see also *Abstr.*, 1898, i, 485; Tutin and Kipping, *Trans.*, 1904, **85**, 65), consists of two stereoisomeric bases, which are separated by fractional precipitation from the ethereal solution by means of formic acid, the formate of α -dimethylcyclohexylamine being thrown down before that of the β -stereoisomeride.

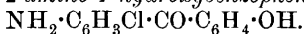
α -Dimethylcyclohexylamine is obtained as an oil, which boils at 273° and forms with water a solid *hydrate*; this melts at 46—48° and liquefies, losing water over sulphuric acid in a desiccator. The *hydrochloride* melts at 285°. The *benzoyl* derivative, $N(C_7H_{13})_2Bz$, crystallises from alcohol in plates, melts at 141°, and has $[\alpha]_D -34.646^\circ$; the *nitroso-derivative*, $C_{14}H_{26}ON_2$, crystallises from methyl alcohol, melts

at 83—84°, and has $[\alpha]_D - 34^\circ$; the *phenylcarbamyl* derivative, $N(C_7H_{13})_2 \cdot CO \cdot NPh$, melts at 174—176°.

β -Dimethylcyclohexylamine is obtained as an oil which boils at 273° and does not form a hydrate; the *hydrochloride* melts at 211°; the *nitrate* and the *nitrite* are sparingly soluble. The *benzoyl* derivative melts at 151° and has $[\alpha]_D - 11.877^\circ$; the *nitroso*-derivative, melting at 62—70°, and the *phenylcarbamyl* derivative, melting at 137—138°, have smaller molecular rotations than the corresponding α -derivatives. G. Y.

Action of *o*-Nitrobenzaldehyde on Phenols in Presence of Hydrogen Chloride. THEODOR ZINCKE and K. SIEBERT (*Ber.*, 1906, 39, 1930—1938. Compare Zincke and Preuntzell, this vol., i, 110; Schillinger and Wleügel, *Abstr.*, 1884, 60).—4-Chloro-2-*p*-hydroxyphenylanthroxan, $C_6H_3Cl \left\langle \begin{smallmatrix} C(C_6H_4 \cdot OH) \\ N \end{smallmatrix} \right\rangle O$, is prepared by saturating a solution of *o*-nitrobenzaldehyde and phenol in glacial acetic acid or methyl or ethyl alcohol, cooled by ice, with hydrogen chloride, or by the action of phosphorus oxychloride on the glacial acetic acid solution; it crystallises in yellow needles, melts at 241°, sublimes without decomposition when heated carefully, is readily soluble in alcohol or acetic acid, but is only sparingly so in ether or benzene, and dissolves in aqueous sodium hydroxide, forming an orange-yellow solution. The dilute alcoholic solution becomes strongly fluorescent on addition of ammonia or an alkali hydroxide. The *acetyl* derivative, $C_{18}H_{17}O_2ClNAc$, crystallises in broad, colourless needles and melts at 171°.

Reduction of the anthroxan by hydriodic acid and phosphorus leads to the formation of 5-chloro-2-amino-4'-hydroxybenzhydrol, or by tin and hydrochloric acid in alcoholic or glacial acetic acid solution to the formation of 5-chloro-2-amino-4'-hydroxybenzophenol,



This crystallises in glistening, colourless needles, melts at 174°, and dissolves readily in alcohol, in glacial acetic acid forming a red, or in aqueous alkali hydroxides forming a yellow, solution. The *nitrate* and *sulphate* are readily soluble, but the *hydrochloride*, which crystallises in yellow needles, is insoluble in dilute acids. The *diacetyl* derivative, $C_{17}H_{14}O_4NCl$, crystallises in stout, white needles or leaflets and melts at 140°. The action of nitric acid of sp. gr. 1.5 on the amine leads to the formation of an unstable *product*, which is probably a mixture of two nitro-derivatives. When diazotised and coupled with β -naphthol, the amine yields a red *dye*; when boiled, the diazonium sulphate solution evolves nitrogen and yields a *product* which is soluble in aqueous alkali hydroxides; the diazonium chloride is reduced by stannous chloride, forming a yellow precipitate which resinifies when filtered. The *perbromide*, $C_{13}H_6OClBr_3$, prepared from the diazonium chloride, crystallises in red needles and melts at 198°.

5-Chloro-4'-hydroxybenzophenone, $C_6H_4Cl \cdot CO \cdot C_6H_4 \cdot OH$, formed by the action of amyl nitrite on the amine, crystallises in white needles, melts at 161°, and dissolves readily in alcohol, glacial acetic acid, or

aqueous alkali hydroxides. The *acetyl* derivative, $C_{15}H_{11}O_3Cl$, crystallises in white needles and melts at 108° .

5-Chloro-4'-hydroxybenzhydrol, $C_6H_4Cl \cdot CH(OH) \cdot C_6H_4 \cdot OH$, is prepared by reduction of the ketone by means of sodium amalgam in dilute alkaline solution; it crystallises in white needles and melts at 125° .

4-Chloro-2-p-hydroxy-m-tolylantrioxan, $C_6H_3Cl \cdot \underset{N}{\overset{C(C_7H_6 \cdot OH)}{>O}}$, formed from *o*-nitrobenzaldehyde and *p*-cresol, crystallises from alcohol in light yellow needles and melts at 210° ; the *alkali* salts crystallise in glistening, orange-yellow leaflets. The *acetyl* derivative, $C_{16}H_{12}O_3NCl$, crystallises in white, glistening leaflets and melts at 135° .

5-Chloro-2-amino-2'-hydroxy-4'-methylbenzophenone,
 $NH_2 \cdot C_6H_3Cl \cdot CO \cdot C_6H_3Me \cdot OH$,
 formed by reduction of the anthroxan by tin and hydrochloric acid, crystallises in yellow needles, melts at 115° , and dissolves in aqueous alkali hydroxides, forming yellow solutions; the *sodium* salt crystallises in glistening, golden leaflets. The *hydrochloride* forms colourless needles and is hydrolysed by water. The *diacetyl* derivative,

$C_{18}H_{12}O_4NCl$,
 crystallises in yellow needles and melts at 151° . The action of ethyl nitrite on the amine leads to the formation of a *substance* which separates from alcohol in yellow crystals, and when heated with nitric acid of sp. gr. 1.4 yields 7-chloro-1:9-dinitro-2-methylacridone. This is formed also by treatment of the amino-compound with nitric acid of sp. gr. 1.4; it crystallises in glistening, yellow needles, melts at 250° , and is insoluble in aqueous, but dissolves in aqueous-alcoholic sodium hydroxide, forming a deep red solution, which deposits the *sodium* salt in violet needles, decomposed by water. G. Y.

Action of Benzene and Aluminium Chloride on Free Phenol-carboxylic Chlorides. RICHARD ANSCHÜTZ (*Annalen*, 1906, 346, 381—391.)—[With JEFF H. SHORES.]—3:5-Dichloro-2-hydroxybenzophenone, $OH \cdot C_6H_2Cl_2 \cdot CPh$, is prepared by heating 3:5-dichlorosalicylic chloride with aluminium chloride and benzene in a reflux apparatus and treating the product with dilute hydrochloric acid; it crystallises from alcohol in yellow needles, melts at 116° , is readily soluble in cold benzene or hot alcohol, but dissolves to only a slight extent in water, forming a yellow solution, and with aqueous sodium hydroxide forms a reddish-yellow solution of the *sodium* derivative.

The action of phenylhydrazine on the ketone leads to the formation of (a) the *phenylhydrazone*, $OH \cdot C_6H_2Cl_2 \cdot CPh \cdot N \cdot NHPh$, which crystallises from 96 per cent. alcohol in stellate aggregates of yellow needles, melts at 186° , and is insoluble in water, and (b) the *phenylhydrazonium* derivative of the phenylhydrazone,

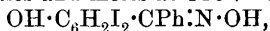
$NHPh \cdot N^+ : CPh \cdot C_6H_2Cl_2 \cdot O \cdot NH_3 \cdot NHPh$,
 which crystallises from benzene in long, white, woolly needles. The *oxime*, $OH \cdot C_6H_2Cl_2 \cdot CPh \cdot N \cdot OH$, crystallises in light yellow, silvery needles and melts at 196° .

3:5-Dichloro-2-hydroxybenzhydrol, $OH \cdot C_6H_2Cl_2 \cdot CHPh \cdot OH$, prepared

by reduction of the ketone with 3 per cent. sodium amalgam in alcoholic solution, crystallises from light petroleum in thin, white needles and melts at 94° .

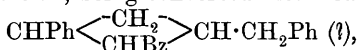
[With EMANUEL LÖWENBERG.]—3:5-Dibromo-2-hydroxybenzophenone, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{COPh}$, formed by the action of aluminium chloride and benzene on 3:5-dibromosalicylic chloride, crystallises in long, yellow needles, melts at $129\text{--}130^{\circ}$, dissolves in aqueous sodium hydroxide forming a yellowish-green solution, and when treated with phenylhydrazine forms two phenylhydrazones. The stable *phenylhydrazone*, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CPh}\cdot\text{N}\cdot\text{NHPh}$, crystallises from dilute alcohol in yellow rhomboids and melts at $176\text{--}177^{\circ}$. The labile *modification*, which separates from the concentrated mother liquor from the stable form in white crystals, melts and resolidifies, changing into the stable modification at 143° . The labile *oxime*, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CPh}\cdot\text{N}\cdot\text{OH}$, formed by the action of hydroxylamine on the ketone in alcoholic solution, crystallises in white needles and melts and resolidifies at 175° , changing into the stable *oxime* which melts at $199\text{--}201^{\circ}$.

[With FRITZ SCHMITZ.]—3:5-Di-iodobenzophenone, $\text{OH}\cdot\text{C}_6\text{H}_2\text{I}_2\cdot\text{COPh}$, formed from 3:5-di-iodosalicylic chloride, crystallises from alcohol in glistening, golden needles and melts at 116° . The *oxime*,



crystallises in slightly yellow needles and melts at 127° . G. Y.

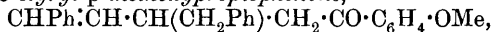
Action of a 50 per cent. Mixture of Glacial Acetic and Sulphuric Acids on β -Benzyl- β -styrylpropiophenone and its Derivatives. HUGO BAUER and ERNST BREIT (*Ber.*, 1906, 39, 1916—1921. Compare Bauer, *Abstr.*, 1905, i, 278; Kohler, *ibid.*, 358).—When heated on the water-bath with a mixture of equal parts of glacial acetic and sulphuric acids, β -benzyl- β -styrylpropiophenone undergoes isomerisation, being converted into a *substance*,



which crystallises from alcohol in colourless leaflets, melts at 117° , and remains unchanged when treated with potassium permanganate in acetone solution, but is oxidised slowly to carbon dioxide by aqueous permanganate at 100° . When heated with potassium hydroxide at 300° , it yields benzoic acid and an *acid*, $\text{C}_{17}\text{H}_{18}\text{O}_2$, which crystallises in slender, white needles, melts at $169\cdot5\text{--}170^{\circ}$, and is readily soluble in alcohol; the *barium* salt was analysed. The *oxime*, $\text{C}_{24}\text{H}_{22}\cdot\text{N}\cdot\text{OH}$, crystallises from alcohol and melts at 166° ; the *bromo*-derivative, $\text{C}_{24}\text{H}_{21}\text{OBr}$, crystallises in colourless needles and melts at $161\cdot5^{\circ}$.

Cinnamylidene-p-methoxyacetophenone, $\text{C}_{18}\text{H}_{16}\text{O}_2$, prepared by shaking *p*-methoxyacetophenone with cinnamaldehyde in aqueous sodium hydroxide solution, crystallises in light yellow needles, melts at $95\cdot5\text{--}96\cdot5^{\circ}$, is readily soluble in alcohol, ether, or acetone, and gives a cherry-red coloration with concentrated sulphuric acid. The *oxime*, $\text{C}_{18}\text{H}_{17}\text{O}_2\text{N}$, crystallises in colourless, glistening, silky leaflets, melts at $131\cdot5^{\circ}$, and is readily soluble in alcohol.

β -Benzyl- β -styryl-p-methoxypropiophenone,

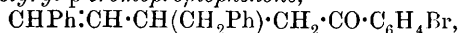


is prepared by adding ice-water to a mixture of the cinnamylidene-

compound and magnesium benzyl chloride in ethereal solution; it is obtained as a viscid oil, which solidifies under alcohol, forming white needles, melts at 82.5° , and gives a yellowish-green coloration with concentrated sulphuric acid. When heated with glacial acetic and sulphuric acids, it is converted into an *isomeride*, $C_{25}H_{24}O_2$, which forms glistening, white needles, melts at 125° , and is readily soluble in alcohol or acetone.

Cinnamylidene-p-bromoacetophenone, $C_{17}H_{13}OBr$, prepared from cinnamaldehyde and *p*-bromoacetophenone, crystallises from acetone in light yellow, matted needles and melts at 149.5° . The *oxime* forms colourless, silky leaflets and melts at 184.5 — 185.5° .

β -Benzyl- β -styryl-p-bromopropiophenone,



separates from alcohol in white crystals, melts at 114° , and is readily soluble in alcohol or ether. The *isomeride*, $C_{24}H_{21}OBr$, crystallises in colourless leaflets and melts at 112° . G. Y.

Constitution of α - and β -Benzopinacolins. MAURICE DELACRE (*Bull. Acad. roy. Belg.*, 1906, 62—70).—A critical *résumé* is given of the known facts regarding the chemistry of the two benzopinacolins (Abstr., 1891, 456; 1896, i, 662; Klinger and Lonnes, Abstr., 1896, i, 691; and Werner and Grob, Abstr., 1904, i, 864), and it is pointed out that the data at present available are insufficient to permit of a formula being definitely assigned to each of these two substances. The author is of opinion that only one benzopinacolin exists and that the variations in structure are not due, as he and others have supposed, to isomerisation induced by the action of reagents, but to an equilibrium phenomenon. T. A. H.

Constitution of Tribenzoylenebenzene. ARTHUR MICHAEL (*Ber.*, 1906, 39, 1908—1915).—The constitution originally assigned to tribenzoylenebenzene is the correct one; truxene (tribenzylenebenzene) and allied compounds are derivatives of benzene and not of tetrane.

The preparation of tribenzoylenebenzene from the sodium derivative of ethyl 1:3-diketohydrindenecarboxylate is described.

The identity of tribenzoylenebenzene prepared from 1:3-diketohydrindene with that prepared from phthalylacetic acid is based essentially on the similarity in physical properties.

The anhydride, $C_{18}H_{10}O_3$, prepared by the action of phosphorus oxychloride on phenylpropionic acid according to Lanser, is identical with the product which Michael and Bucher obtained by the action of acetic anhydride on phenylpropionic acid. When this anhydride is dissolved in alkali, it readily forms salts of the dibasic acid, $C_{18}H_{12}O_4$, and when the alkaline solution is acidified, the acid separates and not the anhydride, as Michael and Bucher originally supposed. The acid, $C_{18}H_{12}O_4$, is moderately stable and does not form an appreciable amount of anhydride when heated at 100° ; anhydride formation takes place rapidly at 155 — 165° .

Phenylnaphthalenedicarboxylic acid (Lanser's "diphenyltetrenedicarboxylic acid") is shown to be quite distinct from phenenyltribenzoic acid.

The solubility of the acids in alcohol, glacial acetic acid, and ether respectively is different; the difference between the acids is also indicated by the comparison of their salts quoted. Further, a fluorescein is formed when phenylnaphthalenedicarboxylic acid is fused with resorcinol; phenenyltribenzoic acid does not form a fluorescein. α -Phenylnaphthalene may be isolated from phenylnaphthalenedicarboxylic acid by heating a mixture of the barium salt with barium hydroxide, whilst the hydrocarbon resulting from phenenyltribenzoic acid is triphenylbenzene.

A. McK.

Preparation of Amino-, Alkylamino-, and Arylamino-anthraquinones and their Derivatives. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 165728).—1-Dimethylamino-5-phenoxyanthraquinone, $\text{NMe}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{C}(\text{CO})_2 \cdot \text{C}_6\text{H}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_5$, prepared by heating the di-

phenyl ether of anthrarufin with a 10 per cent. solution of dimethylamine in pyridine at 110 — 115° , separates from alcohol in red crystals and melts at 147 — 149° .

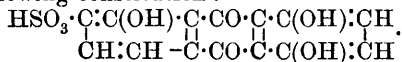
1-Dimethylamino-8-phenoxyanthraquinone, which separates from alcohol in thick crystals melting at 127 — 128° , is obtained similarly from the diphenyl ether of chrysazin. This ether also gives rise to 1-phenylamino-8-phenoxyanthraquinone, which crystallises from pyridine in long, lustrous needles and melts at 173 — 174° .

This patent contains several other examples of the substitution of a phenoxy-group by a substituted amino-radicle. In two instances, two amino-groups were introduced into the aromatic nucleus. Thus, 1-phenoxyanthraquinone-5-sulphonic acid when heated with solutions of methylamine and ammonia gave rise to 1:5-dimethyldiaminoanthraquinone and 1:5-diaminoanthraquinone respectively.

G. T. M.

Preparation of Polyhydroxyanthraquinonesulphonic Acids. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 165860).—When the polyhydroxyanthraquinones are sulphonated according to the usual processes, mixtures of sulphonic acids are produced which are difficult to separate, and, moreover, oxidation readily occurs with the introduction of more hydroxyl groups (compare this vol, i, 294). The result is quite different in the presence of boric acid. In this case, homogeneous products are obtained without oxidation.

1:4:5-Trihydroxyanthraquinone, mixed with an equal weight of boric acid, is treated with twenty parts of fuming 30 per cent. sulphuric acid, at 130° ; the product when poured into water gives the free sulphonic acid which is transformed into its acid sodium salt, which separates in orange-red crystals. The new sulphonic acid has probably the following constitution:



Alizarin-bordeaux when sulphonated in this way also gives rise to a monosulphonic acid.

G. T. M.

Presence of *l*-Borneol in the Ethereal Oil from the Buds of *Pinus maritima*. E. BELLONI (*Chem. Centr.*, 1906, i, 1552; from *Boll. Chim. Farm.*, 45, 185—187).—The presence of *l*-borneol in the oil from *Pinus maritima* has been detected by the method X of Tiemann and Krüger (*Abstr.*, 1896, i, 382). In the following table, the physical constants and composition of four samples of oil are given: I and II were prepared from fresh buds, and III and IV partly from dried buds.

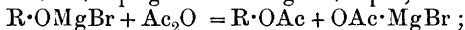
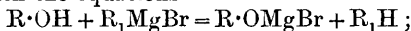
	I.	II.	III.	IV.
Yield from buds	0.856	0.867	0.841	0.892
Sp. gr. at 15°	0.8797	0.8805	0.889	0.8848
[α] _D at 15°	-29.4°	-30.48°	-24.45°	-26.17°
<i>n</i> _D at 20°	1.4795	1.4812	1.482	1.478
Free acid calculated as octoic acid...	0.30 %	0.28 %	0.97 %	0.59 %
Esters as bornyl acetate	1.58	1.12	1.67	1.37
Free alcohol (<i>l</i> -borneol)	5.08	6.78	5.19	7.83
Combined alcohol	1.25	0.89	1.31	1.07
Total alcohol	6.33	7.67	6.50	8.90

E. W. W.

Chemistry of Bornyl- and Fenchyl-alcohols. IWAN L. KONDAKOFF (*Chem. Zeit.*, 1906, 30, 497—499). Compare *Abstr.*, 1904, i, 755).—A critical discussion regarding the probable constitution of these substances.

P. H.

Esterification of Alcohols and Phenols. JOSEF HOUBEN (*Ber.*, 1906, 39, 1736—1753).—The Grignard reagents are employed, in accordance with the equations



Magnesium alkyl bromides give satisfactory results in the case of saturated primary aliphatic alcohols or phenols, but the unsaturated alcohols, geraniol, linalool, and terpineol, in these circumstances, yield esters which are coloured, contain halogen, and quickly resinify. With such alcohols better results are obtained with magnesium benzyl chloride, but best of all with magnesium alkyl chlorides, when the reaction proceeds almost quantitatively and the ester obtained after fractionation is colourless, free from halogen, and does not exhibit any tendency to become resinous. The operation is performed as follows: the alcohol is slowly added to the cold ethereal solution containing magnesium ethyl or methyl chloride in excess of the theoretical quantity; after keeping at the ordinary temperature for twelve to twenty-four hours, the mixture is well cooled and an excess of acetic anhydride added drop by drop. After one hour, the mixture is decomposed by ice and acetic acid, the ethereal layer removed, dried over potassium carbonate, and the ester fractionated under reduced pressure after evaporation of the ether.

Linalyl propionate is a colourless liquid with an odour of lilies of the valley, and boils at 108—111° under 12 mm. or at 115—119° under 16 mm. pressure.

Terpinyl propionate is a pleasant-smelling liquid which boils at 119—121° under 11.5 mm. pressure. *Cis*-terpin yields a *diacetate*,

which boils at 140—141° under 10 mm. pressure and has only a faint odour, differing in these respects from Oppenheim's terpin diacetate (*Annalen*, 1864, **129**, 157), which is probably a mixture of terpinyl acetate, acetic acid, and dipentene, into which the diacetate decomposes when distilled under the ordinary pressure. The terpinyl acetate obtained from this mixture is a different substance from that obtained directly from terpineol.

C. S.

Preparation of the Terpinoid Alcohol, Nerol. HEINE & CO. (D.R.-P. 165894, 165895, 165896. Compare this vol., i, 295).—Nerol is prepared from linalool by the following series of operations: the latter oil was dissolved in glacial acid, treated in the cold with concentrated sulphuric acid dissolved in the same solvent, the oily product washed with water and hydrolysed with alcoholic potash on the water-bath. The hydrolysed oil was distilled in steam and then fractionated under reduced pressure; the less volatile products, consisting of terpineol, geraniol, and nerol, were boiled with phthalic anhydride and benzene, whereby the primary alcohols only were converted into the corresponding acid phthalates. After removing the excess of unchanged anhydride by cooling and adding light petroleum, the solution was distilled and the residual acid phthalates dissolved in dilute aqueous sodium carbonate. The alkaline solution was washed with ether, acidified with dilute sulphuric acid, and the acid phthalates extracted with ether and hydrolysed with alcoholic potash at the ordinary temperature or on the water-bath. The resulting alcohols, geraniol and nerol, were distilled in steam or under diminished pressure and finally separated by means of dry calcium chloride, which yields with geraniol a compound insoluble in light petroleum. The yield of rectified nerol was about 5—10 per cent.

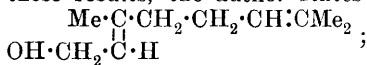
The initial esterification can be accomplished likewise with acetic anhydride, the yield by this method being 15—20 per cent. Other acetylating agents may be employed, such as acetic acid with sodium acetate, ferric chloride, or phosphoric acid. Linalyl acetate and the ethereal oils containing this ester are also amenable to this process of separation.

G. T. M.

Nerol and its Preparation from Linalool. OTTO ZEITSCHSEL (*Ber.*, 1906, **39**, 1780—1792).—When *l*-linalool (Barbier's licarhodol, *Abstr.*, 1893, i, 544) is treated with acetic anhydride, formic acid, or sulphuric and acetic acids (Stephen, *Abstr.*, 1899, i, 68), nerol can be isolated in quantities varying from 3 to 10 per cent.; dilute mineral acids act on linalyl acetate to give a similar poor yield of nerol.

When an alcoholic solution of citral is reduced with sodium amalgam, the resinifying action of the alkali being prevented by the addition of acetic acid drop by drop, geraniol and nerol are produced to the extent of 12 and 7 per cent. respectively. The oxidation of nerol or geraniol by chromic and sulphuric acids yields citral and a substance with the odour of methylheptenone.

Basing his conclusions mainly on these results, the author states that geraniol has the constitution



nerol, $\text{Me} \cdot \underset{\text{H} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{OH}}{\underset{|}{\text{C}}} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} : \text{CMe}_2$; and that citral *a* is identical with geranial and citral *b* with nerol.

Terpin hydrate was isolated from the products of the reaction between nerol or geraniol and 5 per cent. sulphuric acid after two hundred hours' shaking (Tiemann, Abstr., 1895, i, 639). The acetates are practically unchanged by this treatment, whilst the linalyl ester is converted more slowly into terpineol and terpin hydrate. C. S.

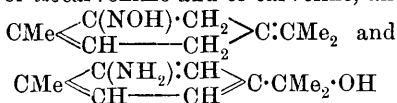
Identity of Natural and Artificial Nerols. HUGO VON SODEN and WALTER TREFF (*Ber.*, 1906, 39, 1792—1793. Compare preceding abstract).—Nerol, obtained from linalool and freed as much as possible from geraniol by calcium chloride, is converted into the diphenylurethane, which is crystallised from light petroleum (Abstr., this vol., i, 295). The recovered nerol agrees in all its properties and in the characteristics of its compounds with the alcohol obtained from natural sources. C. S.

Preparation of the Hydrates of Unsaturated Organic Compounds. KNOLL & Co. (D.R.-P. 165726).—*Citronellidineacetone hydrate* was obtained by boiling together citronellidineacetone and sodium hydrogen sulphite in aqueous solution, then adding dilute acid, and leaving the mixture for several days, after which the intermediate bisulphite compound was decomposed by sodium hydroxide. The hydrate thus liberated when fractionated under reduced pressure boiled at 175° under 12 mm. pressure.

Carvone hydrate was similarly produced by the successive action of sodium hydrogen sulphite, dilute sulphuric acid, and sodium hydroxide; it boils at 153—154° under 12 mm. pressure and melts at 43°. Its semicarbazone melts at 177° and its oxime at 113°.

Ethyl citrylidenemalonate hydrate, obtained in a similar manner from ethyl citrylidenemalonate, boils at 215—225° under 12 mm. pressure and has a sp. gr. 1.022 at 20°. G. T. M.

Terpenes and Ethereal Oils. LXXX. isoCarvoxime and the Constitution of Carvoline. Remarks on the Mechanism of the Isomerisation of Oximes. OTTO WALLACH (*Annalen*, 1906, 346, 266—285. Compare Goldschmidt and Kisser, Abstr., 1887, 475, 923; Goldschmidt, Abstr., 1893, i, 723).—The author discusses the constitution of *isocarvoxime* and of *carvoline*, and ascribes to these the formulæ



respectively; the formation of the latter from the former is compared with that of aminothymol from carvoxime. These changes, which resemble that of phenylhydroxylamine into aminophenol, may be explained by the Beckmann reaction, if this is considered to take place through the intermediate formation of a nitrogen heterocyclic group.

[With HERMANN LAUTSCH.]—*iso*Carvoxime was prepared by shaking carvoxime with hydrogen bromide in glacial acetic acid solution and heating the product with sodium methoxide in methyl-alcoholic solution. With bromine it forms a *dibromide*, $C_{10}H_{15}ONBr_2$, melting and decomposing at 126—127°, and a *tetrabromide*, $C_{10}H_{15}ONBr_4$, melting at 134—135°.

Carvoline (Goldschmidt, *loc. cit.*) is formed together with carvacrol when *isocarvoxime* is boiled with dilute sulphuric, acetic, or oxalic acid; it crystallises in colourless needles or prisms, boils at 158—163° under 12 mm. or at 289—290° under the ordinary pressure, and is not volatile in a current of steam; the *hydrochloride* melts at 189—190°. When boiled with fuming hydriodic acid in a reflux apparatus, the base yields carvacrylamine. Carvoline forms dyes when diazotised and coupled with phenols: the *product* with β -naphthol, $OH \cdot C_{10}H_{12}N_2 \cdot C_{10}H_7O$, crystallises in deep red needles, melts at 171°, and is insoluble in aqueous alkali hydroxides. The *diazonium sulphate* obtained from carvoline is decomposed by boiling water, forming a *phenol* which yields a deep yellowish-brown dye when coupled with diazotised sulphanilic acid in alkaline solution. The *chloro-derivative*, $CMe \begin{smallmatrix} \text{CCl} \cdot \text{CH} \\ \text{CH} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot CMe_2 \cdot OH$, formed from carvoline by Sandmeyer's reaction, melts at 50—51°, boils at 245—249°, when treated with phosphorus pentachloride yields an oily *dichloride*, boiling at 230—234°, and is oxidised by chromic acid to *o-chloro-p-acetyltoluene*, $C_6H_3MeCl \cdot CMe$. This has an odour of acetophenone, melts at 45—46°, boils at 250—254°, and is volatile in a current of steam. The crystalline *semicarbazone* melts at 237—238°; the *oxime*, $C_6H_3Cl \cdot CMe \cdot N \cdot OH$, forms white leaflets and melts at 96—97°. When treated with a hypobromite solution, the ketone is oxidised to *o-chloro-p-toluic acid*. G. Y.

Synthesis of Camphor Derivatives. *iso*Laurolene and *iso*-Lauronolic Acid (β -Campholytic Acid). GUSTAVE BLANC (*Compt. rend.*, 1906, 142, 1084—1086).— $\alpha\alpha$ -Dimethyladipic acid was prepared as already described (Abstr., 1905, i, 680), except that ethyl γ -bromo- $\alpha\alpha$ -dimethylbutyrate, $CH_2Br \cdot CH_2 \cdot CMe_2 \cdot CO_2Et$, was condensed with ethyl malonate in place of ethyl sodiocyanoacetate. The acid was warmed with acetic anhydride and the resulting anhydride converted by distillation into *dimethylcyclopentanone*, $\begin{smallmatrix} CH_2 \cdot CH_2 \\ | \quad | \\ CH_2 - CO \end{smallmatrix} > CMe_2$. This is a mobile liquid, has a camphoraceous odour, and melts at 143°; its *semicarbazone* melts at 190°. The ketone on treatment with magnesium methyl iodide yields the *tertiary alcohol*, $\begin{smallmatrix} CH_2 \cdot CMe_2 \\ | \quad | \\ CH_2 - CH_2 \end{smallmatrix} > CMe \cdot OH$, which crystallises in long needles, melts at 37°, boils at 60° under 15 mm. pressure, and possesses a musty, camphoraceous odour. When distilled under atmospheric pressure, it decomposes into water and *iso*-laurolene, $\begin{smallmatrix} CH_2 \cdot CH_2 \\ | \quad | \\ CH = CMe \end{smallmatrix} > CMe_2$. The hydrocarbon is transformed by condensation with acetyl chloride in presence of aluminium chloride

into a *ketone*, which is reduced by sodium to the secondary *alcohol*, $\text{CMe}_2 \cdot \text{CHMe} \begin{matrix} \text{CH}_2 \\ \text{CH}_2 \end{matrix} \text{---} \text{CH}_2 \text{---} \text{CH}_2 \text{---} \text{CH} \cdot \text{CHMe} \cdot \text{OH}$, which boils at 90—95° under 10 mm. pressure, and this on oxidation by nitric acid gives dihydroisolauronic acid, which on bromination in the α -position and subsequent elimination of hydrogen bromide gives isolauronic acid.

T. A. H.

Ethereal Oils. HEINRICH HAENSEL (*Chem. Centr.*, 1906, i, 1497; from *Geschäftsber.*, March, 1906. Compare Abstr., 1903, i, 187).—Silver fir oil from Lower Austria has almost the same sp. gr. as the Tyrolese oil, but it has a less rotatory power and contains a smaller quantity of esters; it has sp. gr. 0·8761—0·8776 at 15°, $[\alpha]_D$ -35·99° to -37·14° at 15°, and contains 4·46—5·22 per cent. of esters calculated as bornyl acetate. The fruit from which the seeds have been removed yields 0·038 per cent. of an orange-coloured oil which has a strong odour of the fruit and an acid reaction: it has a sp. gr. 0·90735 at 20°, $[\alpha]_D$ +0·40° at 19° (10 per cent. benzene solution), and acid number 22·1. The oil contains aldehydes, and a stearoptene is precipitated on the addition of absolute alcohol.

Dried garden rue yields 0·135 per cent. of a dark brown, ethereal oil which has a very strongly acid reaction and on rectification forms a pale greenish-yellow oil, which has a sp. gr. 0·8487 at 20°, $[\alpha]_D$ +0·64° at 20°, and ester number 119; the acetyl derivative has ester number 157. When shaken with a solution of sodium hydrogen sulphite, the oil does not yield an additive compound.

E. W. W.

Ethereal Oils. SCHIMMEL & Co. (*Chem. Centr.*, 1906, i, 1497—1498; from *Geschäftsber.*, April, 1906. Compare Abstr., 1905, i, 536).—Lemon-yellow cedar oil from Haiti has an odour similar to that of ordinary cedar oil, sp. gr. 0·9612 at 15°, $[\alpha]_D$ -14°58', acid number 2·7, and ester number 5·0; the acetyl derivative has ester number 64. Fennel oil contains camphene and phellandrene, but not cymene (compare Tardy, Abstr., 1897, i, 578). Templin oil prepared from Styrian material has a sp. gr. 0·8685 at 15°, $[\alpha]_D$ -11°3', acid number 1·4, and ester number 16·8 (=5·9 per cent. bornyl acetate); 67 per cent. of the oil distils at 170—203°. Styrian silver fir oil has sp. gr. 0·8852 at 15°, $[\alpha]_D$ -34°55', and ester number 17·5 (=6·1 per cent. bornyl acetate); 55 per cent. of the oil distils at 162—185°. Two black pine oils prepared from needles of *Pinus Laricio* have sp. gr. 0·8646 and 0·8701 at 15°, $[\alpha]_D$ +8°17' and +3°29', and ester numbers 2·9 and 9·8 respectively. Bay-leaf oil contains linalool and the methyl ether of eugenol. Bright yellow sassafras oil prepared from the roots of *Sassafras officinalis* dissolves in 1—2 volumes of 90 per cent. alcohol, and has a sp. gr. 1·075 at 15°, $[\alpha]_D$ +2°14', and ester number 1·9. Solidago oil, or oil of Golden Rod, is pale yellow, and has a pleasant, refreshing odour; it has a sp. gr. 0·8904 at 15°, $[\alpha]_D$ +15°34', and ester number 34·2 (acetyl derivative 59·9). The esters probably consist mainly of bornyl acetate. The bright olive-green oil from *Solidago nemoralis* has a peculiar odour, resembling that of

cypress oil; it has a sp. gr. 0.8799 at 15°, $[\alpha]_D - 23^{\circ}10'$, and ester number 14.4 (acetyl derivative 38.2). Indian turpentine oil from the resinous balsam of *Pinus longifolia* is soluble in 7.5 volumes of 90 per cent. alcohol, and has a sp. gr. 0.8734 at 15°, $[\alpha]_D + 3^{\circ}13'$, acid number 1.9, and ester number 1.3.

An ethereal oil which contains free fatty acids and constituents which cannot be saponified is obtained by extracting musk with ether and distilling in steam. The odour of musk is caused by the presence of a ketone, *muskone*, $C_{15}H_{28}O$ or $C_{16}H_{30}O$, which boils at 327—330° and at 142—143° under 752 and 2 mm. pressure respectively; it has sp. gr. 0.9268 at 15°, $[\alpha]_D - 10^{\circ}6'$, and n_D 1.47900 at 25°. The *semicarbazone* melts at 133—134°. E. W. W.

Ethereal Oil of the Buds of *Pinus maritima*. E. BELLONI (*Chem. Centr.*, 1906, i, 360—361; from *Ann. Soc. Chim. Milano*, ii).—The fresh buds of *Pinus maritima* collected in S. France yield on distillation 0.517 per cent. of a bright green ethereal oil, which has a fresh, aromatic taste and the characteristic odour of pine needles; the dry buds yield 0.681 per cent. of a similar oil. The following data refer respectively to the oil from the fresh buds and to that from the dry buds. Sp. gr. at 15°, 0.8810 and 0.8963; $[\alpha]_D$ at 15°, $-26^{\circ}518'$ and $-22^{\circ}355'$; acid numbers, 0 and 5.43; ester numbers, 7.90 and 8.27; saponification numbers, 7.90 and 13.70; esters, 2.77 and 2.92 per cent.; combined alcohols, 2.13 and 2.28 per cent. The oil from the dried buds also contained 11.90 of uncombined alcohols and a total of 14.18 per cent. of alcohols. The oil is miscible with 95—100 per cent. alcohol, is soluble in 10 parts of 90 per cent. alcohol, but insoluble in 80 per cent. alcohol, and does not contain aldehydes. The free acids consist mainly of hexoic acid, of which the oil contains 1.396 per cent., and the esters appear to be acetates, propionates, hexoates, and laurates. *l*-Pinene is the chief constituent of the oil. When the alcoholic solution of *l*-pinene nitrosochloride is heated with piperidine for a long time on the water-bath, needle-shaped crystals of nitrosopinene separate from the product after some days. Neither phellandrene nor silvestrene could be detected in the fraction of the oil boiling at 170—190°, but limonene appeared to be present either in the form of one of the two active modifications or in the inactive form as dipentene. Although the odour of the oil indicates the presence of ethers of borneol, attempts to isolate these compounds from the fractions boiling at 190—260° failed. E. W. W.

The Constituents of the Gutta-percha from *Palaquium treubi*. ÉMILE JUNGFLEISCH and HENRI LEROUX (*Compt. rend.*, 1906, 142, 1218—1221).—The crude gutta of the leaves of *Palaquium treubi* contains a crystalline principle, *paltreubin*, $C_{30}H_{50}O$, which remains dissolved when the hot toluene extract of the leaves is treated with alcohol in order to precipitate the hydrocarbon of the gutta, and is separated by evaporating the mother liquor to dryness, extracting the wax from the residue by means of hot alcohol, and finally recrystallising from benzene. *Paltreubin* forms colourless, silky needles belonging to the monoclinic system (Wyrouboff), it melts at 260°, and

sublimes at 230° , forming characteristic elongated prisms; it is almost insoluble in all the ordinary organic solvents except toluene or benzene, and its solutions are optically inactive. Paltreubin is completely esterified when heated with excess of acetic anhydride in sealed tubes at 175° ; the product consists of two isomeric acetates from which two alcohols, each isomeric with the original, are obtained by saponification.

α -Paltreubyl acetate, $C_{30}H_{49}\cdot OAc$, melts at 235° , is soluble in ether, and can be recrystallised from benzene in the form of voluminous crystals or monoclinic prisms (Wyrouboff); its solutions are optically inactive, and it yields α -paltreubyl alcohol, $C_{30}H_{49}\cdot OH$, on saponification with alcoholic potassium hydroxide, which crystallises from benzene in needles melting at 190° . β -Paltreubyl acetate, $C_{30}H_{49}\cdot OAc$, melts at 290° , is sparingly soluble in ether, crystallises from benzene in well-developed, colourless prisms belonging to the monoclinic system, but different from those of the α -isomeride (Wyrouboff); β -paltreubyl alcohol, $C_{30}H_{49}\cdot OH$, obtained from the preceding compound by saponification with alcoholic potassium hydroxide, crystallises from benzene in long, thin needles, melts at 295° , and sublimes at 270 — 275° , forming thin, prismatic needles, and is identical with an alcohol which the authors have extracted from the leaves of *P. gutta* or *P. borneese*, or from a residue obtained in the commercial preparation of gutta from leaves.

Paltreubin and α - and β -paltreubyl alcohol are isomeric with α - and β -amyrin (Vesterberg, Abstr., 1887, 733; 1891, 165). M. A. W.

Sapotoxin and Sapogenin from *Agrostemma githago*. JOSEF BRANDL [with E. MAYR and A. VIERLING] (*Chem. Centr.*, 1906, i, 1350—1353; from *Arch. exp. Path. Pharm.*, 54, 245—284).—The seeds of *Agrostemma githago* contain 6.44 per cent. of fat and yield 4.9—6.1 of crude sapotoxin. 18.1 per cent. of pure sapotoxin is obtained from the crude product by extraction with absolute alcohol, the insoluble residue consisting of a higher sapotoxin. The pure sapotoxin is dull brownish-yellow and contains C 54.23 per cent., H 7.23, and O 38.54; it forms a bright yellow solution in water, and the rotatory power of a 2 per cent. solution in a 20 cm. tube is $+0.22^{\circ}$. A determination of the molecular weight by Raoult's method gave 1810. Sapogenin, prepared by digesting sapotoxin with dilute sulphuric acid, contains 66.28 per cent. of carbon, 8.62 of hydrogen, and 25.10 of oxygen, crystallises from absolute alcohol in very small, slender needles, becomes yellow at 190° , sinters at 210° , and decomposes at 220° ; it is a saturated acid and liberates carbon dioxide from carbonates. The rotatory power of a 2 per cent. solution in sodium carbonate solution in a 20 cm. tube is $+1.6^{\circ}$. Molecular weight determinations by Raoult's method gave 605 and 648, and by the boiling point method 643 and 662. 51.92 per cent. of a sugar (calculated as dextrose) is also formed by the hydrolysis of sapotoxin; it is inactive, is scarcely attacked by yeast in twenty-four hours, and forms three osazones melting respectively at 180° , 203° , and 205° . By the action of acetic anhydride on sapogenin, an acetyl derivative which crystallises from methyl alcohol is formed, together with a by-product which is soluble in water, gives a precipitate with lead acetate,

but has no hæmolytic action. The potassium and sodium salts of sapogenin crystallise in slender needles, and the potassium salt of methylsapogenin in very slender rods.

Sapogenin, $C_{33}H_{52}O_{10}$, prepared by the action of dilute sulphuric acid on quillajic acid or on quillajasapotoxin, crystallises from absolute alcohol in slender, white needles; a determination of the molecular weight by the boiling-point method gave 561.

The physiological action of *Agrostemma* sapotoxin and sapogenin is also described in some detail in the abstract. E. W. W.

Products extracted from *Solanum sodomaeum*. II. GIUSEPPE ODDO and AMEDEO COLOMBANO (*Gazzetta*, 1906, **36**, i, 310—313. Compare Abstr., 1905, i, 455).—The authors describe a method for extracting solanine from *Solanum sodomaeum* more simply and in better yield than by the process formerly described (*loc. cit.*). The berries are well pounded in a marble mortar and are then macerated for twenty-four hours with sufficient 2·5 per cent. sulphuric acid solution to cover them completely. The solution is then filtered through flannel, the filtrate rendered alkaline with sodium or potassium hydroxide solution and the precipitated solanin filtered through flannel, washed well with water, dried, and treated with alcohol as previously described.

The neutralised acid extract is found to contain also a compound which crystallises from water in aggregates of small, reddish-yellow prisms, beginning to melt at 195° and completely melting and decomposing at 215° . Its aqueous solution is coloured green by ferric chloride solution and an intense blood-red by alkali. Alkali carbonate solutions dissolve it, giving brownish-yellow liquids. T. H. P.

Solanine and other Constituents of the Berries of *Solanum sodomaeum* from Sicily. ARTURO SOLDAINI (*Chem. Centr.*, 1906, i, 563; from *Boll. Chim. Farm.*, 1905, **44**, 769—773, 808—810, and 843—885).—The author concludes that neither he nor Oddo and Colombano (Abstr., 1905, i, 455) have yet been dealing with the pure alkaloid (glucoside), and therefore many of his previously published results require modification. P. H.

Aloxanthin. OTTO A. OESTERLE (*Chem. Centr.*, 1906, i, 367—368; from *Schweiz. Woch. Pharm.*, **43**, 682—684. Compare Abstr., 1899, i, 538).—Alochrysin is not a homogeneous compound, since the acetyl derivative can be separated into two components, of which the one is insoluble in benzene and a derivative of rhein, whilst the other is a derivative of aloemodin. It is probable that emodin is first formed by the action of potassium dichromate and sulphuric acid on aloin and is then oxidised to rhein. It should doubtless be possible to obtain emodin in this way. E. W. W.

Condensation Products of Tannic Acid with Formaldehyde and Acid Amides. ARNOLD VOSWINKEL (D.R.-P. 165980).—The condensation products of tannic acid with formaldehyde and acid amides have the general formula $C_{14}H_9O_5 \cdot CH_2 \cdot NH \cdot COR$.

The formamide derivative, $C_{16}H_{18}O_{10}N$, which was prepared by adding formaldehyde and formamide to a solution of tannic acid in dilute hydrochloric acid, forms a light brown powder insoluble in water or alcohol.

Methylene-tannin-acetamide, $C_{17}H_{19}O_{10}N$, was obtained similarly and resembles the preceding compound. The derivatives of amides sparingly soluble or insoluble in water were prepared in alcoholic solutions. These products are all soluble in aqueous solutions of sodium carbonate, borate, or acetate, and are regenerated on treatment with acids. The compounds have therapeutic properties similar to those of the carbamide derivatives.

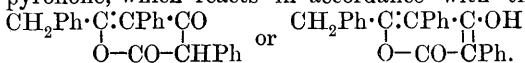
G. T. M.

Constitution of Methronic Acid. HYPOLYT TREPHILIEFF (*Ber.*, 1906, 39, 1859—1862. Compare Fittig and Hantzsch, *Abstr.*, 1889, 126).—Ethyl methronate does not react with phenylhydrazine; the acid is oxidised by nitric acid to acetic and oxalic acids, combines with four atoms of bromine, and is hydrolysed to acetonylacetone. Under Fittig's conditions of preparation, 40 per cent. of the sodium succinate remains in the mother liquor without any ethyl acetoacetate, and the yield is only 30 per cent. of the theoretical; this is increased to 58 per cent. when 2 mols. each of ethyl acetoacetate and acetic anhydride are used for each mol. of sodium succinate. The by-products in the reaction are carbon dioxide, ethyl acetate, and acetone.

In accordance with these facts, methronic acid is regarded as having the formula $\begin{array}{c} C(CO_2H) \equiv CMe \\ CH:C(CH_2 \cdot CO_2H) > O. \end{array}$

C. S.

Synthesis of Simple Pyronones from Acid Haloids. EDGAR WEDEKIND (*Chem. Centr.*, 1906, i, 369; from *Verh. Deut. Naturforsch. Aerzte*, 1904, ii, 81—83. Compare *Abstr.*, 1901, i, 639; 1902, i, 739).—When propionyl, phenylacetyl, or hydrocinnamoyl chloride acts on tertiary bases, the acid chloride residues unite to form trimeric condensation products. Hydrocinnamoyl chloride yields benzyldiphenyl pyronone, which reacts in accordance with the tautomeric formulæ



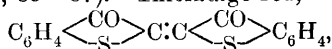
The pyronone forms a sodium salt when treated with sodium hydroxide, and an oxime with hydroxylamine. By the action of acyl chlorides, acyl derivatives are obtained, and benzyldiphenyl dihydroxy-

pyridine, $\begin{array}{c} CH_2Ph \cdot \overset{\overset{O}{\parallel}}{C} - CPh - \overset{\overset{O}{\parallel}}{C} \cdot OH \\ | \\ N:C(OH) \cdot CPh \end{array}$, is formed by the action of ammonia.

When isobutyl chloride acts on tertiary bases, a diketone of the tetramethylene series seems to be produced.

E. W. W.

Thioindigo-red B. R. WIRTHEK (*Chem. Centr.*, 1906, i, 1353; from *Färberzeit.*, 17, 85—87).—Thioindigo-red,



manufactured by Kalle & Co., of Biebrich, resembles indigo in its method of application as a dye, its solubility in concentrated sulphuric

acid, and its slight solubility in organic solvents. It can be sublimed, and its solutions in chloroform, carbon disulphide, toluene, &c., have a yellowish-red fluorescence. Wool, silk, and cotton extract the colouring matter from the yellow solution formed by the action of reducing agents on the dye, and the red dye is regenerated when the fibres are exposed to air. Thioindigo-red may be used with a sodium sulphide bath, and may also be applied in cotton printing. E. W. W.

Constitution of Adrenaline. ERNST FRIEDMANN (*Beitr. chem. Physiol. Path.*, 1906, 8, 95—120. Compare Abstr., 1904, i, 1069; also Takamine, Abstr., 1902, ii, 217; Aldrich, 1901, ii, 564; 1902, ii, 518; Abel, *ibid.*, 1903, i, 376; von Fürth, *ibid.*, 669; Pauly, 1904, i, 128, 540; Jowett, Trans., 1904, 85, 192; Bertrand, Stolz, 1905, i, 106).—A modified method for the preparation of von Fürth's adrenaline tribenzenesulphonate is described. In chloroform solution it has $[\alpha]_D -15.12^\circ$, but the rotation is somewhat less after it has been warmed with acetic acid. The presence of a free hydroxyl group has been shown by its conversion into the *m*-nitrobenzoate, $C_{34}H_{28}O_{12}N_2S_3$, which is doubly refracting. It begins to sinter at 71° and melts between 80° and 86° .

When adrenaline tribenzenesulphonate is oxidised with an acetic acid solution of chromic anhydride, it yields *adrenalone tribenzenesulphonate*, $(SO_2Ph \cdot O)_2C_6H_3 \cdot CO \cdot CH_2 \cdot NMe \cdot SO_2Ph$, which may be purified by solution in acetic acid and precipitation with water. It dissolves sparingly in cold benzene or ethyl acetate and in hot alcohol, and is insoluble in ether, acids, or alkalis. It is optically inactive, and may be crystallised from acetic acid at 0° , and then separates from absolute alcohol in long, rhombic needles melting at 106 — 107° . Its *p*-nitrophenylhydrazone, $C_{33}H_{28}O_{10}N_4S_3$, melts at 174 — 175° .

The substance previously termed peradrenalone tribenzenesulphonate is shown to be a mixture of adrenalone and a more complex substance melting at 196 — 197° . It dissolves in ammonium hydroxide solution.

Adrenalone tribenzenesulphonate has been synthesised from methyl-aminoacetylcatechol. J. J. S.

Quinine Tannate. MAXIMILIAN NIERENSTEIN (*Chem. Centr.*, 1906, i, 1417; from *Collegium*, 1906, 108).—*Quinine tannate* forms a white, amorphous powder which melts at 64° ; it separates from a solution in alcohol to which 4—5 drops of acetic anhydride are added in crystals which melt at 79 — 81° . Since neither tannin nor gallic acid is formed when the tannate is hydrolysed, it cannot be a true salt, but is possibly a compound resembling a Schiff's base. E. W. W.

Action of Gum Arabic on Morphine. RICHARD FIRBAS (*Chem. Centr.*, 1906, i, 374; from *Pharm. Post.*, 38, 735—738. Compare Bourquelot, *J. Pharm. Chim.*, [vi], 19, 475).—An oxymorphine is formed by the action of a solution of gum arabic on morphine, although comparatively slowly, the action being dependent on the concentration of the solution and the time. If the quantity is not too small, the presence of oxymorphine may be detected by the precipitate which it gives with potassium chromate. The gum does

not appear, however, to have any action on opium powder or extract even when the substances are allowed to remain together in a moist condition for six weeks.

E. W. W.

Morphine Alkylbromides. J. D. RIEDEL (D.R.-P. 165898).—*Morphine methobromide*, prepared by shaking together for eight to twelve hours at 40–50° a mixture of finely-divided morphine, methyl bromide, and absolute alcohol, was recrystallised from water or dilute alcohol and separated in colourless needles, sintering at 260° and melting at 265–266°. It is only sparingly soluble in absolute alcohol or chloroform, and is insoluble in ether. The same salt was also obtained when finely-divided morphine was suspended in a mixture of chloroform and methyl sulphate, and shaken at the ordinary temperature for one day, when the methosulphate separated. This salt was dissolved in water and treated with concentrated aqueous potassium bromide or any other soluble bromide, when the required methobromide was precipitated.

Morphine ethobromide was obtained from the corresponding ethiodide by treating the latter with moist silver bromide; it crystallises from water or alcohol in colourless needles melting at 245°. These quaternary salts have the narcotic action of morphine, but are far less poisonous.

G. T. M.

The Alkyl Bromides of the Alkyl Ethers of Morphine. J. D. RIEDEL (D.R.-P. 166362).—*Codeine methobromide*, $C_{19}H_{24}O_3NBr$, which is a white, crystalline powder melting at 261°, can be obtained by any of the following processes: from codeine and methyl bromide in dry chloroform, alcoholic, or acetone solution; by double decomposition from the methosulphate and lead bromide; by the methylation of morphine methobromide with sodium ethoxide and methyl bromide.

Codeine ethobromide, $C_{20}H_{26}O_3NBr$, produced from the corresponding ethiodide by the action of moist silver bromide, crystallises from acetone in lustrous needles, which contain acetone of crystallisation; these sinter at 70° and melt at 74°. When dried at 100–120°, the substance loses acetone, and then melts at 244–245°.

Codethyline methobromide, $C_{20}H_{26}O_3NBr \cdot H_2O$, is obtained either by evaporating a solution of codethyline methylammonium hydroxide with hydrobromic acid or by treating the methochloride (obtained either from the iodide with moist silver chloride or from the methosulphate with potassium chloride) with saturated aqueous potassium bromide; it crystallises in needles, which, after drying at 120°, melt at 267–268°.

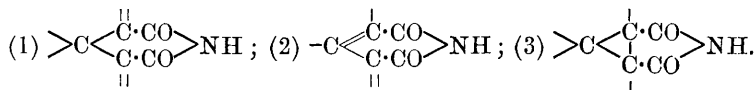
Codethyline ethobromide, $C_{21}H_{28}O_3NBr$, produced by ethylating morphine at 80° with ethyl bromide and alcoholic potash, crystallises in soft, lustrous needles containing 3 or 4 H_2O ; after dehydrating, it melts at 225°.

G. T. M.

Products of Hydrogenation of Pyrrole by means of Reduced Nickel. MAURIZIO PADOA (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 219–223).—By passing a mixture of pyrrole vapour and hydrogen

through a tube containing reduced nickel (from the reduction of nickel carbonate in hydrogen at 350°) at 180—190°, the author obtains: (1) a 25 per cent. yield of pyrrolidine, and (2) a small quantity of a hexahydroindoline (?), which gives a *picrate*, $C_8H_{15}N, C_6H_3O_7N_3$, crystallising from alcohol in yellow needles melting at 123°. T. H. P.

Invertive Power of Certain Pseudo-acids having Complex Functions. RODOLFO TORRESE (*Atti R. Accad. Sci. Torino*, 1906, 41, 309—327).—The author has examined, with regard to their capability of hydrolysing sucrose, a number of derivatives of glutaconimide having formulæ represented by the following schemes:

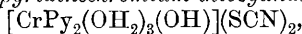


Compounds of types (1) and (3) are unable to hydrolyse sucrose, whilst those of type (2) are able to do so. In order, therefore, that they may exhibit this property, the molecules must possess a double linking in the position shown in (2), and they must, further, have the two carbonyl groups unsubstituted; if, for instance, one of the carbonyl groups is replaced by CMe_2 , the power to invert sucrose is lost.

T. H. P.

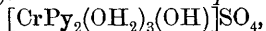
A New Class of Salt-forming Metallic Hydroxides. PAUL PFEIFFER [with M. TAPUACH and W. OSANN] (*Ber.*, 1906, 39, 1864—1879. Compare *Abstr.*, 1902, i, 728).—*Dihydroxylodiaquodipyridinechromium bromide*, $[CrPy_2(OH_2)_2(OH)_2]Br$ (where $Py = C_5NH_5$), is prepared by the addition of pyridine or of ammonia to an aqueous solution of the tetra-aquobromide, $[CrPy_2(OH_2)_4]Br_3$ (*loc. cit.*).

Hydroxylotriaquodipyridinechromium thiocyanate,



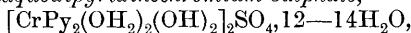
prepared from ammonium thiocyanate and tetra-aquodipyridinechromium chloride, forms violet-red crystals; its aqueous solution is greyish-green.

Hydroxylotriaquodipyridinechromium sulphate,



prepared by the addition of pyridine or of ammonia to an aqueous solution of the hydrogen sulphate, $[CrPy_2(OH_2)_4](SO_4)_2H$, forms a green solution with an excess of water.

Dihydroxylodiaquodipyridinechromium sulphate,



prepared by the action of ammonia on tetra-aquodipyridinechromium sulphate, forms greyish-violet crystals. It may also be formed from the trihydroxylo-compound by the careful addition of sulphuric acid. When sulphuric acid is added in excess to dihydroxylodiaquodipyridinechromium sulphate, the latter is converted into the monohydroxylo-sulphate, which then passes into the hydrogen tetra-aquosulphate. When an aqueous solution of dihydroxylodiaquodipyridinechromium sulphate is decomposed by ammonia, the trihydroxylo-compound is formed.

Chromiumtrihydroxyloaquodipyridine, $[\text{CrPy}_2(\text{OH}_2)(\text{OH})_3] \cdot 6\text{H}_2\text{O}$, prepared by the action of concentrated ammonia on the dihydroxylo-sulphate or by the action of concentrated ammonia on the mono-hydroxylosulphate, or by the action of ammonia on a mixture of the dihydroxylochloride and the dihydroxylobromide suspended in water, forms glistening, violet crystals and is insoluble in water. It forms red solutions with dilute mineral acids.

The corresponding dihydroxylo-salts are produced by the action of a little hydrochloric, hydrobromic, or sulphuric acid on an aqueous emulsion of the trihydroxyl compound in question. By the action of an excess of concentrated hydrochloric acid on the trihydroxyl compound, tetra-aquodipyridinechromium chloride is formed. Chromiumtrihydroxyloaquodipyridine is very unstable, undergoing partial decomposition when exposed to air at the ordinary temperature. A green residue is left when the compound is exposed in a desiccator containing phosphoric oxide or when it is kept under diminished pressure, water and pyridine being evolved in each case.

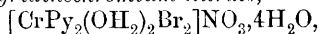
Chromiumdichlorohydroxyloaquodipyridine, $[\text{CrPy}_2(\text{OH}_2)(\text{OH})\text{Cl}_2]$, was prepared as follows. The green product obtained by heating tetra-aquodipyridinechromium chloride in a sealed tube (compare succeeding abstract) was triturated with dilute hydrochloric acid, and to the solution remaining after filtration from chromiumtrichloro-aquodipyridine pyridine was probably added, when chromiumdichloro-hydroxyloaquodipyridine was precipitated. It is a green microcrystalline powder which decomposes on prolonged exposure to the air at the ordinary temperature and is insoluble in water. Its solutions in dilute mineral acids are green. When suspended in water and ammonia then added, it forms the compound, $[\text{CrPy}_2(\text{OH}_2)_2(\text{OH})_2]\text{Cl}$, which, by the action of concentrated hydrochloric acid, is converted into tetra-aquodipyridinechromium chloride, $[\text{CrPy}_2(\text{OH}_2)_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$.

The constitution of the substances enumerated is discussed. The hydroxy-groupings are directly attached to the chromium atom. The compounds described form salts with acids by direct addition and not by substitution.

A. McK.

Hydrate Isomerism with Chromium Salts. PAUL PFEIFFER [and M. TAPUACH] (*Ber.*, 1906, 38, 1879—1896).—When the violet-red tetra-aquodipyridinechromium bromide, $[\text{CrPy}_2(\text{OH}_2)_4]\text{Br}_3 \cdot 2\text{H}_2\text{O}$, where $\text{Py} = \text{C}_5\text{NH}_5$ (compare Abstr., 1902, i, 728), is allowed to remain for several weeks in a closed vessel, it assumes a green tint. When heated in a closed vessel for three hours at 60—65°, it is converted into the green isomeride, *dibromodiaquodipyridinechromium bromide*, $[\text{CrPy}_2(\text{OH}_2)_2\text{Br}_2]\text{Br} \cdot 4\text{H}_2\text{O}$;

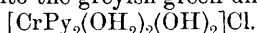
the latter forms a green solution with ethyl alcohol or methyl alcohol. As distinguished from the violet-red isomeride, it does not form a clear solution with water, since it undergoes hydrolytic dissociation with the separation of a green powder (possibly $[\text{CrPy}_2(\text{OH}_2)(\text{OH})\text{Br}_2]$). When an excess of pyridine is added to a solution of the dibromobromide in water containing hydrochloric acid, a green precipitate of the pseudobase, $[\text{CrPy}_2(\text{OH}_2)(\text{OH})\text{Br}_2]$, is formed; the latter is very labile and is quickly transformed into the basic bromide of the tetra-aquo-series.

Dibromodiaquodipyridinechromium nitrate,

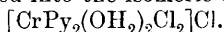
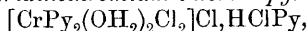
prepared from nitric acid and dibromodiaquodipyridinechromium bromide, forms dark green needles. It does not form a clear solution with water owing to partial separation of the hydroxylobromocompound, which can be dissolved by the addition of mineral acid. When the dibromo-nitrate is added to water, the concentration of bromine ions in the solution remaining after filtration of the hydroxylobromocompound is slight. The compound $[\text{CrPy}_2(\text{OH}_2)_2\text{Br}_2]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ may also be obtained as a bright green, microcrystalline powder by varying the conditions of the interaction between nitric acid and dibromodiaquodipyridinechromium bromide.

Dibromodiaquodipyridinechromium iodide, $[\text{CrPy}_2(\text{OH}_2)_2\text{Br}_2]\text{I} \cdot 4\text{H}_2\text{O}$, prepared by the addition of ammonium iodide to a solution of dibromodiaquodipyridinechromium bromide in hydrochloric acid, separates in dark green needles; its aqueous solution is turbid, on account of the formation by hydrolytic dissociation of a precipitate, probably consisting of the compound $[\text{CrPy}_2(\text{OH}_2)(\text{OH})\text{Br}_2]$; the solution in dilute acids is green. When the salt is heated, iodine is evolved.

Chromium trichloroquodipyridine, $[\text{CrPy}_2(\text{OH}_2)\text{Cl}_3] \cdot \text{H}_2\text{O}$, prepared by heating the violet-red variety of tetra-aquopyridine chromium chloride, $[\text{CrPy}_2(\text{OH}_2)_4]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$, at 75° , and then washing the residue with hydrochloric acid until the filtrate is no longer green, is a yellowish-green powder. In the aqueous solution of the compound, the chlorine is not in the ionic form. When agitated with water and pyridine, the compound is transformed into the greyish-green dihydroxylochloride,

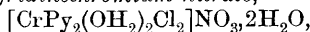


It may also be transformed into the isomeric dichloro-chloride,

*Dichlorodiaquodipyridinechromium chloride pyridinium chloride,*

obtained as a by-product in the preparation of chromiumtrichloroquodipyridine, forms glistening, green needles.

Dichlorodiaquodipyridinechromium chloride, $[\text{CrPy}_2(\text{OH}_2)_2\text{Cl}_2]\text{Cl}$, prepared by the action of concentrated hydrochloric acid on chromiumdichlorohydroxyloquodipyridine (compare preceding abstract), forms glistening, green leaflets; it undergoes hydrolytic dissociation with formation of chromiumdichlorohydroxyloquodipyridine. When exposed at the ordinary temperature, the crystals lose their lustre and hydrogen chloride is evolved.

Dichlorodiaquodipyridinechromium nitrate,

prepared by the action of concentrated nitric acid on chromiumdichlorohydroxyloquodipyridine, forms green needles. In the aqueous solution of the compound, the chlorine is not in the ionic condition.

Dichlorodiaquodipyridinechromium bromide, $[\text{CrPy}_2(\text{OH}_2)_2\text{Cl}_2]\text{Br} \cdot 3\text{H}_2\text{O}$, prepared by the action of hydrobromic acid on chromiumdichlorohydroxyloquodipyridine, forms dark green, prismatic needles.

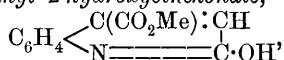
The constitution of these compounds, which are interesting types of isomerism, comparable with Werner's chromium bromide hexahydrates, $[\text{Cr}(\text{OH}_2)_6]\text{Br}_3$ and $[\text{Cr}(\text{OH}_2)_4\text{Br}_2]\text{Br} \cdot 2\text{H}_2\text{O}$, is discussed in the preface.

A. McK.

Preparation of Indoxyl and its Homologues. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 166213, 166214).—A mixture of potassium phenylglycinate, sodium and potassium hydroxides, and magnesium nitride is heated at 220—270° until the fused mass assumes a deep orange or brown colour. The product, when dissolved in water, filtered from magnesium hydroxide, and oxidised, gives a good yield of indigotin.

The phenylglycine employed in this reaction may be replaced by one of its homologues, and any other nitride of the alkaline earths may be substituted for the magnesium compound. A similar result is obtained when calcium carbide or any other alkali or alkaline-earth carbide is employed instead of the nitride. G. T. M.

3-Ethylcinchonic Acid and 2-Hydroxy-3-ethylcinchonic Acid. B. MULERT (*Ber.*, 1906, **39**, 1901—1908. Compare Hübner, this vol., i, 383).—*Methyl 2-hydroxycinchonate*,



prepared by the action of hydrogen chloride on a solution of 2-hydroxycinchonic acid in methyl alcohol, melts at 245°. The corresponding

amide, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C}(\text{CO} \cdot \text{NH}_2) \cdot \text{CH} \\ \diagdown \text{N} = \text{C} \cdot \text{OH} \end{array}$, melts at 357—358°.

2-Chlorocinchonyl chloride, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C}(\text{CO} \cdot \text{Cl}) \cdot \text{CH} \\ \diagdown \text{N} = \text{C} \cdot \text{Cl} \end{array}$, prepared by the action of thionyl chloride on 2-hydroxycinchonic acid, melts at 89—90° and is very stable towards cold water.

2-Chlorocinchonamide, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C}(\text{CO} \cdot \text{NH}_2) \cdot \text{CH} \\ \diagdown \text{N} = \text{C} \cdot \text{Cl} \end{array}$, separates from dilute alcohol in prismatic needles and melts at 234—235°; on further heating it solidifies and again melts at 276—278°.

2-Chlorocinchonanilide, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C}(\text{CO} \cdot \text{NHPh}) \cdot \text{CH} \\ \diagdown \text{N} = \text{C} \cdot \text{Cl} \end{array}$, separates from alcohol in needles and melts at 202°.

Methyl 2-chlorocinchonate, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C}(\text{CO}_2\text{Me}) \cdot \text{CH} \\ \diagdown \text{N} = \text{C} \cdot \text{Cl} \end{array}$, prepared by the addition of 2-chlorocinchonyl chloride to methyl alcohol, melts at 89—90°.

2-Methoxycinchonic acid, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C}(\text{CO}_2\text{H}) \cdot \text{CH} \\ \diagdown \text{N} = \text{C} \cdot \text{OMe} \end{array}$, prepared by the action of sodium methoxide on 2-chlorocinchonic acid, separates from benzene in needles and melts at 178—179°. When heated above its melting point, it is transformed into the isomeric methyl 2-hydroxycinchonate melting at 245—255°. Its *methyl* ester separates from alcohol in needles and melts at 71°.

3-Ethylcinchonic acid, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C}(\text{CO}_2\text{H}) \cdot \text{CH} \\ \diagdown \text{N} = \text{CH} \end{array}$ Et , prepared by the condensation of isatin with butaldoxime in the presence of potassium hydroxide, melts at 222°. Its *sodium* and *silver* salts and its *platinichloride*

were prepared. Its *methyl betaine*, $C_{13}H_{13}O_2N$, prepared by the action of methyl iodide on the silver salt, crystallises in needles and melts at 261° .

3-Ethylcinchoninic chloride hydrochloride, $C_{12}H_{10}ONCl \cdot HCl$, crystallises in needles and melts at $174-175^\circ$.

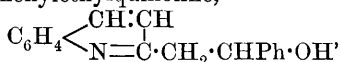
The *amide*, $C_{12}H_{12}ON_2$, separates from water in needles and melts at $220-221^\circ$. The *methyl ester*, $C_{13}H_{13}O_2N$, separates from ether in hexagonal prisms and melts at $37-38^\circ$.

2-Hydroxy-3-ethylcinchoninic acid, $C_6H_4 \begin{smallmatrix} \text{C}(\text{CO}_2\text{H}) \cdot \text{CEt} \\ \text{N} = \text{C} \cdot \text{OH} \end{smallmatrix}$, prepared from isatin and butyric anhydride in presence of aqueous sodium hydroxide, crystallises from water in needles and melts at 285° . Its *sodium* and *silver* salts are described. Its *acid chloride*, prepared by the action of thionyl chloride, separates from chloroform in plates and melts at $194-195^\circ$. Its *methyl ester* melts at 160° ; its *amide* melts at $304-305^\circ$.
A. McK.

Synthesis in Sunlight. ALFRED BENRATH (*J. pr. Chem.*, 1906, [ii], 73, 383—389. Compare Klinger and Standke, *Abstr.*, 1891, 900; Klinger and Kolvenbach, *Abstr.*, 1898, i, 467).—When mixed with *isobutaldehyde*, *salicylaldehyde*, or *benzaldehyde*, and exposed to sunlight, benzil is reduced to benzilbenzoin; anisaldehyde has only a slight, whilst furfuraldehyde, cinnamaldehyde, and valeraldehyde have no reducing action on benzil in sunlight.

1-Benzoyl-1:2-dihydroquinoline, $C_6H_4 \begin{smallmatrix} \text{CH}=\text{CH} \\ \text{NBz} \cdot \text{CH}_2 \end{smallmatrix}$, is formed when benzaldehyde and quinoline are exposed to sunlight; it crystallises in slender, white needles, melts at 200° , is not a base, and is hydrolysed by concentrated hydrochloric acid, forming benzoic acid and 1:2-dihydroquinoline (?); if it is hydrolysed with a hot alkali hydroxide solution, the resulting base is oxidised to quinoline.

2-β-Hydroxy-β-phenylethylquinoline,



formed in the same manner from benzaldehyde and 2-methylquinoline, crystallises from alcohol, melts at 131° , decomposes when heated, forming 2-styrylquinoline, water, 2-methylquinoline, and benzaldehyde, and when boiled with acetic anhydride yields 2-styrylquinoline. The *salts* are only sparingly soluble; the *nitrate* crystallises in yellow, feathery aggregates and melts at 153° ; the *platinichloride*, $(C_{17}H_{15}ON)_2 \cdot H_2PtCl_6$, melts at 232° .

The action of benzaldehyde on cinnamic acid in sunlight leads to the formation of αδ-dibenzoyl-βγ-diphenylbutane.

Benzaldehyde and pyridine do not interact when exposed to sunlight.
G. Y.

Chemical Nature of Methylene-azure. AUGUST BERNTHSEN (*Ber.*, 1906, 39, 1804—1809).—The author discusses the constitution of methylene-azure, and confirms Kehrman's discovery that this substance is a mixture of di- and tri-methylthionine (this vol., i, 460).

Diphenylaminesulphone, $\text{C}_6\text{H}_4\langle\text{NH}\rangle\text{SO}_2\text{C}_6\text{H}_4$, is produced when methyl-diphenylaminesulphone is heated with hydriodic acid, methyl iodide being formed quantitatively. It crystallises in long needles and melts at 257—259°. C. S.

Condensation Products of Rhodanic Acid with Aldehydes. GUIDO BARGELLINI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 181—185. Compare this vol., i, 383).—Reduction of *o*-nitrobenzylidenerhodanic acid (Bondzynski, Abstr., 1887, 1108) by means of ferrous sulphate in ammoniacal solution yields *o*-aminobenzylidenerhodanic acid, which is deposited from aqueous alcohol in blood-red crystals, turning yellow at 200° and decomposing at 265—269°.

m-Nitrobenzylidenerhodanic acid, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{C}\begin{smallmatrix} \text{S} & \text{CS} \\ \diagdown & \diagup \\ \text{CO} & \text{NH} \end{smallmatrix}$, prepared by the action of concentrated sulphuric acid on an alcoholic solution of rhodanic acid and *m*-nitrobenzaldehyde, crystallises from acetic acid in lemon-yellow needles melting and decomposing at 255° and is moderately soluble in benzene, ether, or chloroform, and readily so in alcohol, ethyl acetate, or acetone.

p-Dimethylaminobenzylidenerhodanic acid crystallises from alcohol in minute, blood-red needles, which begin to melt at 240° and are completely melted at about 270° (compare Andreasch and Zipser, Abstr., 1905, i, 930).

p-isoPropylbenzylidenerhodanic acid, $\text{C}_{13}\text{H}_{13}\text{ONS}_2$, prepared from cuminaldehyde and rhodanic acid, crystallises from aqueous alcohol in red needles melting at 154—157°, and is moderately soluble in benzene or ether and readily so in chloroform, acetic acid, or acetone.

4-Hydroxy-2-methyl-5-isopropylbenzylidenerhodanic acid, $\text{C}_{14}\text{H}_{15}\text{O}_2\text{NS}_2$, prepared from thymotic aldehyde and rhodanic acid, forms a mass of orange, woolly crystals melting at 220—221°, and dissolves readily in alcohol, ether, ethyl acetate, acetic acid, or acetone, and to a slight extent in benzene or chloroform.

Thymotic dialdehyde and rhodanic acid give the condensation product, $\text{OH}\cdot\text{C}_6\text{HMePr}_2(\text{CHO})\cdot\text{CH}:\text{C}\begin{smallmatrix} \text{S} & \text{CS} \\ \diagdown & \diagup \\ \text{CO} & \text{NH} \end{smallmatrix}$, which crystallises from alcohol in yellow needles melting at 239—240° and is soluble in ether, ethyl acetate, acetone, or acetic acid, and to a slight extent in benzene.

β -Hydroxynaphthaldehyde and rhodanic acid yield the compound $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}:\text{C}\begin{smallmatrix} \text{S} & \text{CS} \\ \diagdown & \diagup \\ \text{CO} & \text{NH} \end{smallmatrix}$, which crystallises from aqueous alcohol in dark chestnut-red needles blackening at 210° and melting and decomposing at 220°, and dissolves readily in ether, benzene, chloroform, acetone, or acetic acid. T. H. P.

4:5-Diamino-2:6-dihydroxy-3-methylpyrimidine. EMANUEL MERCK (D.R.-P. 166267).—4:5-Diamino-2:6-dihydroxy-3-methylpyrimidine is readily obtained by dissolving 5-isonitroso-4-amino-2:6-

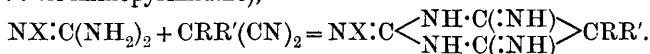
dihydroxy-3-methylpyrimidine in 60 per cent. sulphuric acid and electrolysing the solution in the cathode cell with leaden cathode and a current density of 3 amperes per sq. dm. The liquid is finally saturated with ammonia, when the diamine is set free in a very pure condition. G. T. M.

Preparation of Cyclic Carbamide Derivatives (Pyrimidines). EMANUEL MERCK (D.R.-P. 165561 and 165562).—Carbamide and its alkyl derivatives can be converted into pyrimidine bases by treatment with ethyl cyanoacetate in the presence of an alkali metal or its ethoxide or amide.

4-Amino-2 : 6-dioxypyrimidine, $\text{CO} \begin{smallmatrix} \text{NH} \text{---} \text{CO} \\ \text{NH} \cdot \text{C}(\text{NH}) \end{smallmatrix} \text{CH}_2$, is prepared by the interaction of carbamide, sodamide, and ethyl cyanoacetate in xylene solution.

4-Ethylamino-2 : 6-dioxypyrimidine, obtained by condensing ethyl carbamide and ethyl cyanoacetate in the presence of sodium ethoxide, crystallises in fine needles and possesses both basic and acidic properties. The isonitroso-derivative of this base is a well-defined, violet-red substance melting indefinitely at 278—280°. G. T. M.

Preparation of Derivatives of Barbituric Acid. EMANUEL MERCK (D.R.-P. 165692 and 165693).—Malononitrile and its mono- and di-*C*-alkylated homologues and guanidine and its derivatives undergo condensation to yield derivatives of tri-iminobarbituric acid (2 : 4 : 6-tri-iminopyrimidine),



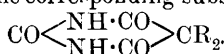
These pyrimidine derivatives are readily hydrolysed to the corresponding barbituric acids, which have a distinctly soporific action.

2 : 4 : 6-Tri-*iminopyrimidine*, melting at 252°, obtained from malononitrile and guanidine in alcoholic solution, yields sparingly soluble salts with the mineral acids and forms a violet nitroso-derivative. The compound from guanidine and ethylmalononitrile melts at 190°. 2 : 4 : 6-Tri-*imino-5 : 5-diethylpyrimidine* melts at 240° and has a strongly alkaline reaction. The compound from methylguanidine and diethylmalononitrile forms cubical crystals and melts at 172°. The compound $\text{C}_9\text{H}_{14}\text{N}_6$, obtained from diethylmalononitrile and either dicyanodiamide or diguanide, melts at 183°.

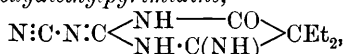
4 : 6-Di-*imino-2-oxy-5-diethylpyrimidine*, melting at 272°, obtained from carbamide and diethylmalononitrile, when boiled with 30 per cent. sulphuric acid yields diethylbarbituric acid. This substance may also be prepared from 2 : 4 : 6-tri-*imino-5 : 5-diethylpyrimidine*, melting at 240°, obtained by condensing diethylmalononitrile with guanidine.

Ethylbarbituric acid (m. p. 194°) is prepared from 2 : 4 : 6-tri-*imino-5-ethylpyrimidine*, melting at 190°, and propylbarbituric acid may be produced from 4 : 6-di-*imino-2-oxy-5-propylpyrimidine*, which decomposes at 300° and is prepared from propylmalononitrile and carbamide in the presence of boiling alcoholic sodium ethoxide. G. T. M.

Preparation of 5:5-Dialkylbarbituric Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 165223).—By the action of dicyanodiamide on dialkylated cyanoacetates, malonates, or dialkylmalononitriles in the presence of alkaline condensing agents, pyrimidine derivatives are produced having the following general formula, $N:C:N:C \begin{smallmatrix} \text{NH} \cdot \text{C}(\text{X}) \\ \text{NH} \cdot \text{C}(\text{X}) \end{smallmatrix} > CR_2$, where R represents alkyl groups and X signifies oxygen atoms or imino-groups. These substances on treatment with acids furnish the corresponding substituted barbituric acids,



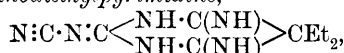
Iminocyanoimino-oxydiethylpyrimidine,



prepared from dicyanodiamide and ethyl diethylcyanoacetate in presence of an alkali ethoxide, separates from water in needles melting at 265° and yields diethylbarbituric acid on boiling with 20 per cent. sulphuric or oxalic acid.

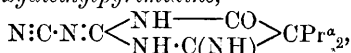
Cyanoiminodioxdiethylpyrimidine, $N:C:N:C \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} > CEt_2$, from dicyanodiamide, ethyl diethylmalonate, and alkali ethoxide, melts at 242° and is readily hydrolysed by 25 per cent. hydrochloric acid.

Di-iminocyanoiminodiethylpyrimidine,



obtained from dicyanodiamide and diethylmalononitrile, melts at 270°.

Iminocyanoimino-oxydiethylpyrimidine,



arising from ethyl dipropylecyanoacetate, melts at 272°, and when hydrolysed with 25 per cent. hydrobromic acid yields 5:5-dipropylbarbituric acid. G. T. M.

Preparation of 5:5-Dialkylbarbituric Acids. ALFRED EINHORN (D.R.-P. 165649).—The 5:5-dialkylbarbituric acids may be obtained from the corresponding thiobarbituric acids by heating with non-oxidising mineral acids. After six to seven hours' boiling with concentrated hydrobromic acid or 33—50 per cent. sulphuric acid, diethylthiobarbituric acid is hydrolysed and dissolved, and pure 5:5-diethylbarbituric acid may be isolated from the product. Hydriodic, hydrochloric, sulphurous, and phosphoric acids may also be employed, and the hydrolysis is accelerated by the addition of alcohol. G. T. M.

Preparation of 2-Arylimino- and 2-Arylhydrazino-5:5-dialkylbarbituric Acids. ALFRED EINHORN (D.R.-P. 166266).—When the thiodialkylbarbituric acids are heated with aromatic amines, sulphur is displaced by the amino-residues and aryliminodialkylbarbituric acids are obtained.

2-Phenyliminodiethylbarbituric acid, which results from the interaction of aniline and thiodiethylbarbituric acid at 120—130°, crystallises from alcohol in white needles or leaflets melting at 253°; when

boiled with mineral acids, it is hydrolysed, yielding aniline and diethylbarbituric acid.

2-Phenylhydrazinodiethylbarbituric acid, obtained under similar conditions from thiodiethylbarbituric acid and phenylhydrazine, is sparingly soluble in methyl and ethyl alcohols, crystallising from the former in yellow leaflets melting at $215-216^{\circ}$; it dissolves in dilute aqueous sodium hydroxide, and the solution passes through a series of colour changes—brown, reddish brown, deep violet, and finally brown again; the liquid at the same time gradually becomes turbid. This hydrazino-derivative is hydrolysed by concentrated mineral acids, phenylhydrazine being eliminated.

2-Phenyliminodimethylbarbituric acid crystallises from alcohol in needles melting at 251° . G. T. M.

Affinity Constants of Cyclic Bases. GEORG DEDICHEN (*Ber.*, 1906, **39**, 1831—1856).—The dissociation constants have been determined of substituted glyoxalines by the conductivity method, of derivatives of pyrazole, triazole, and of *isodihydrotetrazine* by Lowenherz's solubility process, or by the hydrolysis of ethyl formate.

The original paper must be consulted for the tabulated results. In general, the introduction of the methyl or ethyl group affects the affinity of the base to approximately the same extent. The position of the alkyl group has a very marked influence; when it is attached to a nitrogen atom, the effect on the dissociation constant is small, but the affinity of the base is largely increased when an alkyl group is combined with carbon. The introduction of a chlorine atom into 1-methylglyoxaline greatly diminishes the value of *K*. C. S.

Resolution of the Iminazole and Oxazole Rings. OTTO FISCHER (*J. pr. Chem.*, 1906, [ii], **73**, 419—446. Compare Abstr., 1905, i, 245).—[With FRITZ RÖMER].—1-Methyl-, 1-ethyl-, and 1-phenylbenziminazoles are not reduced by sodium and alcohol.

The action of methyl iodide on 2:5-dimethylbenziminazole leads to the formation of 1:2:3:6-tetramethylbenziminazolium iodide and the hydriodides of 1:2:5- and 1:2:6-trimethylbenziminazoles (Fischer and Rigaud, Abstr., 1902, i, 399).

1:2:3:6-Tetramethyl-2:3-dihydrobenziminazole-2-ol (Fischer and Rigaud, *loc. cit.*) sublimes and decomposes only slightly when carefully heated, but decomposes to a marked extent when rapidly heated or distilled. It crystallises from light petroleum in sheaves of needles melting at $148-150^{\circ}$, or from water or very dilute alcohol in plates melting at $166-167^{\circ}$, and distils only slowly in a current of steam. It dissolves in cold acids, and can be reprecipitated immediately by alkali hydroxides or ammonia, but in the acid solution gradually changes into the benziminazolium salt, and is no longer precipitated by ammonia. 1:2:3:6-Tetramethylbenziminazolium picrate melts at $147-148^{\circ}$ (compare Niementowski, Abstr., 1887, 937). The *nitroso-amine*, $\text{NO} \cdot \text{NMe} \cdot \text{C}_6\text{H}_4 \cdot \text{Me} \cdot \text{NMeAc}$, is formed by the action of sodium nitrite on 1:2:3:6-tetramethyldihydrobenziminazole-2-ol in concentrated sulphuric acid solution at 0° ; it crystallises from a mixture of alcohol and light petroleum in long, stout, colourless prisms, melts

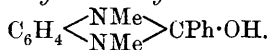
at 71°, becomes yellow or brown in presence of moisture, and gives Liebermann's reaction. The action of alcoholic hydrochloric acid on the nitrosoamine in ethereal solution leads to the formation of 1:2:3:6-tetramethylbenziminazolium chloride.

When heated with sodium hydroxide in alcoholic solution in a sealed tube at 150°, the carbinol or 1:2:3:6-tetramethylbenziminazolium iodide is decomposed, forming 3:4-dimethylaminotoluene, the hydrochloride of which has the formula $C_9H_{16}N_2Cl_2$ (compare Fischer and Rigaud, *loc. cit.*).

The reduction of the carbinol with sodium and alcohol or zinc dust in alkaline solution leads to the formation of 1:2:3:6-tetramethyl-2:3-dihydrobenziminazole, $C_6H_3Me<\begin{smallmatrix} NMe \\ NMe \end{smallmatrix}>CHMe$, which is readily hydrolysed, yielding acetaldehyde and 3:4-dimethylaminotoluene.

When reduced with sodium and alcohol, 1:3:4:6-tetramethyldihydrobenziminazole-2-ol yields formaldehyde and *m*-xylene-4:5-dimethyldiamine, $C_6H_2Me_2(NHMe)_2$. This is obtained as an oil, which boils at 245—250° under 730 mm. pressure, gives with ferric chloride in dilute solution a brownish-red coloration, or in concentrated hydrochloric acid solution a yellow *ferrichloride*, gradually changing into the red *azine* dye, and reacts with formic acid to form 1:3:4:6-tetramethyldihydrobenziminazole-2-ol, or with aldehydes to form unstable dihydrobenziminazoles. The *hydrochloride*, $C_{10}H_{16}N_2 \cdot 2HCl$, crystallises in white, flat prisms. When mixed with salicylaldehyde, the base forms water, and the *condensation product*, $C_{17}H_{20}ON_2$, which crystallises from ether in colourless plates, melts at 132—133° and is hydrolysed to salicylaldehyde and the *o*-diamine when boiled with acids.

2-Phenyl-1:3-dimethylbenziminazolium iodide, $C_{15}H_{15}N_2I$, formed by heating 2-phenylbenziminazole with methyl iodide and methyl alcohol in a sealed tube at 110°, crystallises in white needles, melts at 278—279°, and, when treated with a hot aqueous alkali hydroxide, forms 2-phenyl-1:3-dimethyl-2:3-dihydrobenziminazole-2-ol,



This crystallises in white, tetragonal prisms, melts at 159°, forms a *ferrichloride*, which is readily soluble in water, and with hydriodic acid yields the above benziminazolium iodide, or with alcoholic hydrochloric acid the *chloride*, $C_{15}H_{15}N_2Cl$. When dissolved in dilute hydrochloric acid, cooled by ice, and immediately treated with ammonia, 2-phenyl-1:3-dimethyldihydrobenziminazole-2-ol is regained unchanged, but after twenty to thirty minutes in the acid solution it is converted into the benziminazolium salt, which does not give a precipitate with ammonia. The *picrate* of the carbinol melts at 157—158°. When boiled with alcoholic potassium hydroxide, the carbinol is decomposed and forms *o*-phenylenedimethyldiamine.

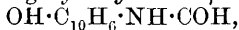
2-Methyl- α -naphthiminazole melts at 171—172° (168—169°; Abstr., 1901, i, 414); when heated with methyl iodide and methyl alcohol in a sealed tube at 140—145°, it forms 1:2:3-trimethyl- α -naphthiminazolium iodide, $C_{14}H_{15}N_2I$, which crystallises in voluminous, white needles, becomes red when dried, melts at 294°, and when treated with aqueous-alcoholic potassium hydroxide yields the *carbinol*,

$C_{10}H_6 \begin{smallmatrix} \text{NMe} \\ \text{NMe} \end{smallmatrix} > CMe \cdot OH$. This crystallises in white, tetragonal prisms, is readily soluble in alcohol, ether, or benzene, forming a solution with violet fluorescence, yields a yellow, crystalline *ferrichloride*, and is converted by acids slowly into the naphthiminazolium salts. The carbinol is very stable towards hydrolysing agents, remaining unchanged when heated with 50 per cent. alcoholic potassium hydroxide at 140–150°, and does not form an azine dye when treated with ferric chloride. The *nitrosoamine*, which is obtained in small yields when the carbinol is treated with sodium nitrite and dilute sulphuric acid cooled by ice, crystallises in slightly yellow plates, melts at 134–135°, and gives Liebermann's reaction.

When heated with methyl iodide and methyl alcohol at 120° in a sealed tube, benzoxazole forms *o*-trimethylaminophenol iodide (Griess, Abstr., 1880, 636). *Benzoxazole methiodide*, $C_6H_4 \begin{smallmatrix} \text{N(MeI)} \\ \text{O} \end{smallmatrix} > CH$, is formed when benzoxazole is heated with an excess of methyl iodide, without methyl alcohol, in a sealed tube at 100°; it crystallises in glistening, yellow needles, melts and evolves iodine at 182–183°, and decomposes when exposed to sunlight. When boiled with concentrated hydrochloric acid, the methiodide is hydrolysed, forming *o*-methylaminophenol.

When heated with methyl iodide at 170°, 2-phenylbenzoxazole yields only a small amount of an impure product containing iodine. Contrary to Hübner's statement (Abstr., 1882, 505), the product of the nitration of 2-phenylbenzoxazole is a *mononitro*-derivative, which, when hydrolysed with concentrated hydrochloric acid, yields benzoic acid. The *picrate*, $C_{13}H_9ON, C_6H_3O_7N_3$, crystallises in matted, yellow needles and melts at 104°.

α -Naphthoxazole, $CH \begin{smallmatrix} C_6H_4 \cdot C \cdot N \\ CH - C \cdot O \end{smallmatrix} > CH$, is prepared by heating *α -amino- β -naphthol* hydrochloride with sodium formate and formic acid in a reflux apparatus; it crystallises in white leaflets, melts at 63.5–64°, and is partially hydrolysed when heated with an aqueous alkali hydroxide. The *platinichloride* is unstable; the *mercurichloride*, $C_{11}H_7ON, HgCl_2$, crystallises in long, colourless, glistening needles and melts at 183–184°; the *picrate*, $C_{11}H_7ON, C_6H_3O_7N_3$, forms needles and melts at 133–134°. The *mononitro*-product, $C_{11}H_6O_3N_2$, formed by the action of cold nitric and sulphuric acids on *α -naphthoxazole*, crystallises in brownish-yellow needles and melts at 135°. When boiled with water in a reflux apparatus for four hours, *α -naphthoxazole* is hydrolysed, yielding *α -formylamino- β -naphthol*,



which crystallises in white, prismatic needles, melts at 204°, and is hydrolysed by boiling concentrated alkali hydroxides, yielding ammonia and *$\alpha\beta$ -dihydroxynaphthalene*. When oxidised with chromic acid in glacial acetic acid solution, *α -naphthoxazole* yields a small amount of an *o*-dicarboxylic acid.

β -Naphthoxazole, $C_{11}H_7ON$, prepared from *β -amino- α -naphthol*, crystallises in stellate groups of slender needles, melts at 79° and is

hydrolysed to only a slight extent by boiling water. When boiled with dilute hydrochloric acid, it is decomposed, forming imino-oxydihydronaphthalene on saturating the solution with ammonia. When boiled with dilute potassium hydroxide, it yields ammonia and $\alpha\beta$ -dihydroxynaphthalene.

Triphenylglyoxaline [lophine], when heated with methyl iodide and methyl alcohol at 120—130°, forms *triphenyldimethylglyoxalinium iodide*, $C_{23}H_{21}N_2I$, which separates from alcohol in white crystals, melts at 266°, and remains unchanged when treated with alcoholic potassium hydroxide. When reduced with sodium and alcohol, it yields benzoic acid, methylamine, and *s*-dimethylstilbenediamine, $C_{16}H_{20}N_2$, which is formed also by hydrolysis of *i*-benzoyl-*s*-dimethylstilbenediamine (Japp and Moir, *Trans.*, 1900, **77**, 608) with concentrated hydrochloric acid at 170—180°. The *hydrochloride* of the diamine, $C_{16}H_{20}N_2 \cdot 2HCl$, was analysed; the *aurichloride*, *platinichloride*, *mercurichloride*, and *picate* are crystalline. The *dinitrosoamine*, $C_{16}H_{18}O_2N_4$, crystallises from acetone in almost colourless, tetragonal prisms, melts at 266—267°, and gives Liebermann's reaction.

The *diacetyl* derivative, $C_{20}H_{24}O_2N_2$, crystallises in white, nodular aggregates and melts at 250—251°. The *dibenzoyl* derivative, $C_{30}H_{28}O_2N_2$, melts at 248—250°.

The *nitroso*-derivative of *i*-benzoyl-*s*-dimethylstilbenediamine melts at 213—215°, and gives Liebermann's reaction. G. Y.

Preparation of Indoxyl and its Derivatives. BASLER CHEMISCHE FABRIK (D.R.-P. 165691).—A convenient process for obtaining indoxyl from phenylglycine consists in adding the potassium salt of the latter to an intimate mixture of potassium hydroxide and sodium oxide (prepared from the metal) heated at 210—260°. The fused mass from ten parts of the alkali phenylglycine derivative when dissolved in water and oxidised by a current of air yielded 4.8 parts of indigo. In this experiment, the phenylglycine may be replaced by its homologues, giving rise to the corresponding indoxyl derivatives.

G. T. M.

Synthesis of Derivatives of Ketoquinazoline. BRONISLAW VON PAWLEWSKI (*Ber.*, 1906, **39**, 1732—1736. Compare *Abstr.*, 1905, i, 246; Kuncell, *Abstr.*, 1905, i, 382).—Anthranilic acid reacts with disubstituted carbamides or thiocarbamides to form only mono-substituted derivatives of ketotetrahydroquinazoline, in the sense of the equation $NH_2 \cdot C_6H_4 \cdot CO_2H + NHR \cdot CO \cdot NHR' = C_6H_4 \begin{smallmatrix} CO-NR \\ \diagup \\ NH \cdot CO \end{smallmatrix} + H_2O + R'NH_2$. Thus, phenylallylthiocarbamide forms 4-keto-2-thion-3-phenyl-1:2:3:4-tetrahydroquinazoline, allylamine, and water.

Molecular quantities of anthranilic acid and allyl thiocarbamide at 150—180° react to form 4-keto-2-thion-3-allyl-1:2:3:4-tetrahydroquinazoline, $C_6H_4 \begin{smallmatrix} CO-N \cdot C_3H_5 \\ \diagup \\ NH \cdot CS \end{smallmatrix}$, which melts at 303—304°, and is oxidised by hydrogen peroxide in alkaline solution to 2:4-diketo-3-allyl-1:2:3:4-tetrahydroquinazoline, which separates from alcohol in needles and melts at 276—278°.

4-Keto-2-thion-1-allyl-1:2:3:4-tetrahydroquinazoline is obtained when a mixture of anthranilic acid and allyl thiocarbimide is heated at 160—165° and finally at 170—180°. It crystallises from alcohol in long prisms, melts at 208—210°, and is oxidised by hydrogen peroxide to *2:4-diketo-1-allyl-1:2:3:4-tetrahydroquinazoline*, which separates from alcohol in long, irregular leaflets and melts at 187—189°.

Anthranilic acid and *o*-tolylthiocarbimide react to form *4-keto-2-thion-3-o-tolyl-1:2:3:4-tetrahydroquinazoline* (compare MacCoy, Abstr., 1897, i, 490; Freundler, Abstr., 1904, i, 830), which crystallises in colourless prisms and needles, melts at 270—271°, and is oxidised by hydrogen peroxide to Busch's *2:4-diketo-3-o-tolyl-1:2:3:4-tetrahydroquinazoline* (Abstr., 1895, i, 307). C. S.

Preparation of Diaminodinaphthazines. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 166363).—The dinaphthazines when dissolved in concentrated sulphuric acid readily yield dinitro-derivatives on nitration; these products on reduction give rise to diaminodinaphthazines, which furnish valuable azo-colouring matters. These diaminodinaphthazines, unlike the aminoazines already described, which contain the amino-group in the para-position, do not exchange this group for hydroxyl on heating under pressure with hydrochloric acid.

$\alpha\beta$ -Dinaphthazine furnishes a *dinitro*-derivative which is very sparingly soluble in all indifferent solvents and crystallises from nitrobenzene in small, yellow needles melting above 300°. This product is reduced to the corresponding *diamino- $\alpha\beta$ -dinaphthazine* by mixing intimately with concentrated sodium sulphide solution and heating the mixture at 90—100°. The diamine is a red substance melting above 300°; it is insoluble in water and sparingly soluble in all organic solvents; its *sulphate* separates from aqueous solutions in very sparingly soluble pale yellow crystals. The compounds obtained under these conditions from $\beta\beta$ -dinaphthazine are quite analogous to the preceding substances. G. T. M.

Condensation Reaction of the Pyrazolones. MARIO BETTI and CURIÒ M. MUNDICI (*Gazzetta*, 1906, 36, i, 178—187).—Pyrazolone reacts with β -hydroxynaphthaldehyde, forming in the first place an unstable, intermediate compound, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}\left(\text{CH}\begin{smallmatrix} \text{CO}-\text{NPh} \\ \text{CMe:N} \end{smallmatrix}\right)_2$, which readily decomposes, yielding methenylbisphenylmethylpyrazolone, $\begin{smallmatrix} \text{NPh}\cdot\text{CO} \\ \text{N}=\text{CMe} \end{smallmatrix} > \text{CH}\cdot\text{CH}:\text{C} < \begin{smallmatrix} \text{CO}-\text{NPh} \\ \text{CMe:N} \end{smallmatrix}$. The reaction evidently depends on the known tendency of the pyrazolones to form the grouping $\text{=CH}\cdot\text{CH}:\text{C=}$. β -Hydroxynaphthaldehyde does not react with methylisooxalazone or with partially substituted pyrazolones or with ethyl malonate; with aromatic amines, it yields anilides and hydrazones.

Methenylbisphenylmethylpyrazolone, $\text{C}_{21}\text{H}_{18}\text{O}_2\text{N}_4$, crystallises in shining, orange-yellow needles melting at 180°, and dissolves moderately well in alcohol and to a slight extent in other organic solvents. It is

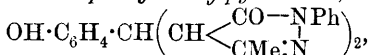
soluble in sodium hydroxide solution and in concentrated sulphuric acid, to which it imparts an intense yellow colour.

The intermediate compound, β -hydroxynaphthylidenebisphenylmethylpyrazolone, $C_{31}H_{26}O_3N_4$, separates in slender, yellow needles melting at 118° to a turbid, yellow liquid which becomes transparent at about 140° ; it cannot be purified, owing to its instability.

Methenylbismethylpyrazolone,
$$\begin{array}{c} \text{NH}-\text{CO} \\ | \\ \text{N}=\text{CMe} \end{array} > \text{CH} \cdot \text{CH} : \text{C} < \begin{array}{c} \text{CO}-\text{NH} \\ | \\ \text{CMe}=\text{N} \end{array}$$
, crystallises from alcohol with EtOH in golden-yellow needles melting at $130-140^\circ$, and dissolves in concentrated sulphuric acid giving a yellow coloration, and in sodium hydroxide solution forming an intensely yellow liquid.

Methenylbisdiphenylpyrazolone,
$$\begin{array}{c} \text{NPh}-\text{CO} \\ | \\ \text{N}=\text{CPh} \end{array} > \text{CH} \cdot \text{CH} : \text{C} < \begin{array}{c} \text{CO}-\text{NPh} \\ | \\ \text{CPh}=\text{N} \end{array}$$
, crystallises from alcohol in reddish-yellow needles and from benzene in orange-yellow needles melting at $249-250^\circ$.

o-Hydroxybenzylidenebisphenylmethylpyrazolone,



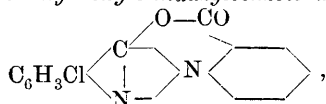
prepared from salicylaldehyde and phenylmethylpyrazolone, crystallises from alcohol in colourless needles melting at $228-230^\circ$, dissolves but slightly in other organic solvents, forms a reddish-yellow solution with concentrated sulphuric acid, and dissolves in sodium hydroxide solution.

Anisylidenebisphenylmethylpyrazolone, $C_{28}H_{25}O_3N_4$, crystallises from alcohol in colourless needles which contain EtOH and melt at 148° , and dissolves in sodium hydroxide solution or concentrated sulphuric acid. T. H. P.

Azo-compounds. Transformation of *o*-Carboxylic Azo-compounds into 3-Hydroxyindazyl Derivatives. PAUL FREUNDLER (*Compt. rend.*, 1906, 142, 1153—1155.—Compare Abstr., 1903, i, 371, 585; 1904, i, 121, 667, 699).—Azo-compounds containing a carboxylic group in the *ortho*-position do not react normally with phosphorus pentachloride, but yield a 3-hydroxyindazyl derivative chlorinated in the ring; thus benzene-*o*-azobenzoic acid yields *chloro-3-hydroxy-2-phenylindazole*, C_6H_3Cl

$$\begin{array}{c} \text{N} \\ | \\ \text{C}_6\text{H}_3\text{Cl} - \text{C} - \text{NPh} \\ | \\ \text{C(OH)} \end{array}$$
, which crystallises in white plates, melts at 265° , is soluble in acetic acid, and almost insoluble in benzene or chloroform, and yields *benzene-*o*-azochlorobenzoic acid*, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{N}_2 \cdot \text{Ph}$, on oxidation with chromic acid or dilute nitric acid, which melts at $124-125^\circ$.

The lactone of *chloro-3-hydroxy-*o*-indazylbenzoic acid*,



obtained by decomposing with water the product of the action of phosphorus pentachloride on *o*-azobenzoic acid, forms thin needles which

melt at 241° , is soluble in benzene, and is converted by nitric acid into chlorodinitrobenzeneazobenzoic acid melting at 225° . M. A. W.

Nitration of 2-Hydroxy-1-diazonaphthalene-4-sulphonic Acid. ANILINFARBEN- & EXTRACT-FABRIKEN VORM. J. R. GEIGY (D.R.-P. 164665).—Well-dried powdered 2-hydroxy-1-diazonaphthalene-4-sulphonic acid dissolved in cold concentrated sulphuric acid was gradually treated at $0-5^{\circ}$ with a mixture of concentrated nitric and sulphuric acids; the mixture was stirred for four hours, allowed to attain a temperature of 15° , and then poured on to ice, when *nitro-2-hydroxy-1-diazonaphthalene-4-sulphonic acid* separated in the form of pale yellow crystals, which can be dried at $80-100^{\circ}$ and are not explosive. The new nitrodiazo-derivative, which is more soluble than the unnitrated compound, readily condenses with phenols to yield azo-colouring matters. G. T. M.

The Electrical Charge of Proteid and its Significance. WOLFGANG PAULI (*Chem. Centr.*, 1906, i, 376—377; from *Naturw. Rundsch.*, 21, 3—5, 17—20).—The serum proteids free from electrolytes have no electrical charge; addition of neutral salts leaves them unchanged, so also does alcohol, which precipitates them readily. Traces of acid or alkali confer on them a positive or negative charge respectively, and hinder their precipitability by alcohol. The differently charged proteids behave in a reverse manner to various ions. The naturally occurring proteids are electro-negative, and the electrical properties of cells and tissues are believed to depend on the charge in their proteid constituents. The similarity between the reactions of colloids and immune substances and between the reactions of the latter substances and fertilisation phenomena is pointed out.

W. D. H.

Optical Rotation and Density of Alcoholic Solutions of Gliadin. W. E. MATHEWSON (*J. Amer. Chem. Soc.*, 1906, 28, 624—628).—An investigation has been made of the variation in the specific rotatory power of gliadin with changes of temperature, concentration, and the nature of the solvent. It has been found that the specific rotation of a solution in 70—75 per cent. alcohol is practically independent of the concentration of the gliadin. Solutions of the proteid in 70—80 per cent. alcohol show a marked increase in specific rotation as the percentage of water in the solvent increases. A rise of temperature between 20° and 45° produces a slight increase in the specific rotation.

Fleurent (*Compt. rend.*, 1901, 132, 1421) has described a method for the estimation of gliadin in flours based on the sp. gr. of the alcoholic extract. It is now shown, however, that the differences in the sp. gr. in such cases are too small to afford accurate results.

E. G.

The Amount of Glycine in Milk Proteids. EMIL ABDERHALDEN and A. HUNTER (*Zeit. physiol. Chem.*, 1906, 47, 404—406).—Skraup

(this vol., i, 123) states that caseinogen contains glycine. This is not the case for the pure substance prepared by Hammarsten's process. The mixed coagulable proteids of milk (lactalbumin and lactoglobulin) yield a small quantity, 1.2 grams of glycine-hydrochloride from 100 grams of the proteid material. Whether this is derived from the albumin or globulin or both is not decided.

W. D. H.

The Monoamino-acids of Legumin. EMIL ABDERHALDEN and BORIS BABKIN (*Zeit. physiol. Chem.*, 1906, 47, 354—358. Compare this vol., i, 56).—Legumin prepared from white beans yields on hydrolysis: glycine, 1; alanine, 2.8; aminovaleric acid, 1; leucine, 8.2; pyrrolidine-2-carboxylic acid, 2.3; phenylalanine, 2; glutamic acid, 16.3; aspartic acid, 4; and tyrosine, 2.8 per cent. The numbers obtained resemble those obtained from conglutin. Conglutin yields 19.5 per cent. of glutamic acid; this corrects a previous statement of the authors, that the yield is low.

W. D. H.

Physical Chemistry of Oxyhæmoglobin. The Capacity for Combining with Alkali of the Colouring Matter of Blood. EMIL ABEL and OTTO VON FÜRTH (*Zeit. Elektrochem.*, 1906, 12, 349—359).—Sodium hydroxide is added to solutions of hæmoglobin, and the concentration of the hydroxyl ions in the resulting solution determined by means of a hydrogen electrode. By comparing the actual concentrations found with those calculated from the quantity of sodium hydroxide added, it is found that 51 mg. of sodium hydroxide are neutralised by one gram of hæmoglobin. The compound is hydrolysed to a considerable extent; if no excess of sodium hydroxide has been added, the hydrolysis amounts to about 18 per cent.

Similar experiments with oxyhæmoglobin were not very successful; the results were not sufficiently definite to admit of any calculation of the concentration of the hydroxyl ions.

T. E.

Action of Quinine on Hæmoglobin. HUGO MARX (*Chem. Centr.*, 1906, i, 1443; from *Arch. exp. Path. Pharm.*, 54, 460—464).—The addition of quinine to blood (fresh or dry) changes the colour to brown, and spectroscopically a well-marked band in the red is seen. Brown crystals separate out; similar results follow the action of quinine on aceto-hæmin crystals. If hæmatoporphyrin hydrochloride is dissolved in a concentrated solution of quinine, the latter substance is precipitated in a crystalline form which carries down the pigment with it.

W. D. H.

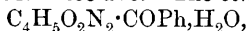
Neuræmin. GABLIN & CIE. (*Chem. Centr.*, 1906, i, 563; from *Pharm. Zeit.*, 1906, 51, 77).—*Neuræmin* is prepared by slowly adding a solution of 10 grams of hæmatin and 10 grams of smilacin in two litres of 90 per cent. alcohol to a solution of 20 grams of lecithin in 100 grams of ether; on distilling off the solvents in a vacuum at 30°, the neuræmin is obtained in the form of a reddish-brown, wax-like solid, which melts at 128° and is readily soluble in alcohol, ether, or acetone.

P. H.

The Cleavage Products of Spongin with Acids. EMIL ABDERHALDEN and EDUARD STRAUSS (*Zeit. physiol. Chem.*, 1906, **48**, 49—53).—In many of the so-called albuminoids (using the term in the limited sense usual among physiologists), typical cleavage products are absent; for instance, tyrosine is absent from gelatin and spongin. Phenylalanine is absent from spongin and keratin. Pyrrolidine-2-carboxylic acid, glycine, and glutamic acid (in large quantities) are obtained from spongin. The transformation of ordinary proteids into such skeletal substances appears to be a result of metabolism and of the action of tissue enzymes. W. D. H.

Decomposition of Histidine. SIGMUND FRÄNKEL (*Beitr. chem. Physiol. Path.*, 1906, **8**, 156—162. Compare Abstr., 1903, i, 650; Pauly, *ibid.*, 1904, i, 1068; Knoop and Windaus, *ibid.*, 1905, i, 834).—*Chlorohistidinecarboxylic acid*, $C_6H_7O_2N_3Cl$, is formed when histidine hydrochloride is treated with nitrous acid at 0° , and the syrup thus obtained reduced with zinc and acetic acid. It crystallises from water in long, transparent plates containing H_2O and melts at 80° . When reduced, it yields *histidinecarboxylic acid* in the form of small crystals, melting at 195° and readily soluble in water. When oxidised with dichromate and sulphuric acid, histidine yields acetic acid and hydrogen cyanide, and when heated at 220° with 20 per cent. hydrochloric acid it yields racemic histidine hydrochloride melting at 220° . When benzoylated by the Schotten-Baumann method, histidine yields a *monobenzoyl* derivative which melts and decomposes at 230° . Even when a large excess of benzoyl chloride is used, no rupture of the ring occurs, and this is regarded as a strong argument against the iminazole formula suggested by Pauly (compare Bamberger and Berlé, Abstr., 1892, 632). Histidinecarboxylic acid cannot be benzoylated. When the hydrochloride of the base is heated above its melting point, carbon dioxide is evolved and a small amount of a compound, $C_4H_6O_2N_3$, can be isolated. Fuming nitric acid reacts with histidine, yielding a yellow, crystalline compound containing water of crystallisation. The anhydrous compound has the composition $C_4H_5O_5N_3$.

Formic acid and a compound, $C_4H_6O_2N_3 \cdot 2H_2O$, which melts at 247° when anhydrous, are formed when histidine is heated with barium hydroxide and water in an autoclave. The *benzoyl* derivative,



melts at 225° .

J. J. S.

Diastatic Saccharification. LÉON MAQUENNE and EUGÈNE ROUX (*Compt. rend.*, 1906, **142**, 1059—1065. Compare this vol., i, 327).—Further experiments on the action of amylase on starch mucilage show that the optimum condition (slightly alkaline liquid) for the production of dextrin is also that which ensures the largest yield of maltose. In a neutral liquid, more maltose may be produced at first, but the reaction stops sooner and the amount of maltose ultimately produced is smaller.

Crude starch contains two products, one readily attacked by amylase and the other (amylopectin) more resistant, but it is also eventually converted into maltose by the enzyme. The neutralisation of amylase

solutions by acids diminishes the stability of the enzyme. The addition of small quantities of acid to starch mucilage undergoing hydrolysis by amylase accelerates the production of maltose, but the addition of further quantities diminishes the activity. Hence it appears probable that amylase occurs in its solutions in combination with a mineral or amino-base forming a kind of zymogen more stable than amylase itself, and that it is liberated from the zymogen by the addition of small quantities of acid.

Solutions of amylase which have been partially neutralised by acid frequently show a change in reaction as saccharification proceeds and tend to revert to the original alkaline condition. The alkali probably results from the decomposition of proteids in the amylase solution by proteolytic enzymes.

T. A. H.

Influence of Chemical Constitution on the Lipolytic Hydrolysis of Esters. JOSEPH H. KASTLE (*Chem. Centr.*, 1906, i, 1536—1537; from *Public Health and Marine-Hospital Service of U.S. Hygienic Lab. Bull.* No. 26, 43—51).—Experiments show that whilst the methyl, ethyl, butyl, *isobutyl*, allyl, and benzyl groups have almost the same effect on the hydrolysis of esters by the action of lipase (from liver), the presence of acyl groups in the homologous series has a considerable influence on the reaction. The quantity of an ester of propionic acid which is attacked in a given time is almost exactly the mean of the quantities of the esters of acetic and butyric acids which are hydrolysed under similar conditions. The action on a formic acid ester is a little more rapid than on an acetic acid ester, but there is practically no difference in the velocity of the action on ethyl butyrate and *isobutyrate*. Experiments with methyl β -iodopropionate, ethyl acetate, and ethyl butyrate show that the introduction of the iodine atom in the β -position does not tend to retard the action of lipase, but rather to accelerate it. The introduction of cyanogen into an ester of acetic acid does not affect the action very considerably, the velocity being reduced at most by half; the retarding influence of the cyanoacetic acid becomes more apparent, however, when the experiment is prolonged.

E. W. W.

Action of Radium Rays on Tyrosinase. EDITH G. WILLCOCK (*J. Physiol.*, 1906, 34, 207—209).—Tyrosinase is an exception to the general rule that radium emanations injure ferments. It may be that the rays bring about oxidation of ordinary ferments, but that oxydase is not itself readily oxidisable, but this view is not strongly urged.

In some cases, where the ferment seemed to be strengthened by exposure to the rays, the result was at first regarded as due to a small amount of hydrogen peroxide formed in the medium. Fenton has shown that radium rays produce this substance from water; this view was not confirmed on examination, for neither glycerol nor water exposed to the rays strengthened the ferment.

W. D. H.

Organic Chemistry.

Volatility in Various Groups of Compounds. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1906, 187—197. Compare Abstr., 1904, i, 466).—*Nitrogen and Phosphorus Compounds.*—The difference between the boiling points of ammonia and hydrogen phosphide is approximately the same as that between the boiling points of hydrazine and liquid hydrogen phosphide. Similarly, the rise in boiling point due to the substitution of H by NH_2 in ammonia is practically the same as that for the replacement of H by PH_2 in hydrogen phosphide.

The replacement of a hydrogen atom by an alkyl group in hydrogen phosphide leads to a greater diminution of volatility than the analogous substitution in ammonia. The replacement of the last hydrogen atom in ammonia by CH_3 leads to an increase in volatility, dimethylamine boiling at 7° and trimethylamine at 3° . In the case of hydrazine, the substitution of an ethyl group for a hydrogen atom leads to an increase of volatility but the effect is less than that due to the substitution of a hydrogen atom by a methyl group. In this respect, hydrazine resembles water, and the phenomenon in both cases is probably due to the fact that water and hydrazine are associated whilst alkyl derivatives are not. The two amino-groups of hydrazine are equivalent so far as the effect of substitution on volatility is concerned.

Carbon and Silicon Compounds.—It is pointed out that of the analogous hydrides, oxides, sulphides, and alkyl derivatives of these two elements, the silicon compounds are, as is to be expected, the less volatile, although this difference tends to disappear, or even to change its sign, in the case of the corresponding alkyloxy-compounds, thus $\text{C}(\text{OEt})_4$ boils at $158\text{--}159^\circ$, whilst $\text{Si}(\text{OEt})_4$ boils at 165° . Among the analogous halogen compounds of the elements, on the other hand, the carbon derivatives are usually the less volatile. This latter fact is not due to difference in degree of association, since several investigators have shown that the two tetrachlorides are associated to about the same extent.

T. A. H.

Use of Metallic Oxides as Catalytic Oxidising Agents. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1906, 142, 1394—1395).—A claim for priority (compare Matignon and Trannoy, this vol., ii, 427). The authors have for some time been engaged on the investigation of the catalytic oxidising action of metallic oxides and find that when a mixture of methane and oxygen is passed over heated copper oxide, the latter becomes incandescent and remains so if the heating is discontinued. The hydrocarbon is almost completely burnt to carbon dioxide and water, a small quantity of formaldehyde and formic acid being formed. Similar results are obtained with pentane, hexane, and heptane, and the copper oxide can be replaced by the oxides of cobalt or nickel.

M. A. W.

Principle of Partition ("Vertheilungsprincip"). ARTHUR MICHAEL (*Ber.*, 1906, 39, 2138—2143).—A theoretical paper, not suitable for abstraction, further elaborating the author's attempt to account for various organic reactions by considering the sum of the influences exerted by all the atoms in the molecule (*Abstr.*, 1900, i, 321).

A. McK.

Application of the Principle of Partition. III. Action of Chlorine on Hexane. ARTHUR MICHAEL and HAROLD J. TURNER (*Ber.*, 1906, 39, 2153—2156. Compare preceding abstract and this vol., i, 551, 559).—When chlorine is passed into boiling hexane in diffused daylight, the resulting mixture of chlorohexanes contains more than 10 per cent. of α -chlorohexane; more β -chlorohexane than γ -chlorohexane is formed.

A. McK.

Preparation of *s*-Tetrachloroethane and Hexachloroethane. FRIEDRICH MICHEL (*Zeit. angew. Chem.*, 1906, 19, 1095—1097).—Disulphur dichloride (S_2Cl_2) mixed with 1 per cent. by weight of reduced iron is saturated with chlorine, the excess of this gas being subsequently removed by a current of carbon dioxide. Dry acetylene is then passed into this liquid, the whole being kept at a temperature of 40°. As soon as the acetylene ceases to be absorbed, the excess is removed by a stream of dry carbon dioxide, and chlorine is once more bubbled through the liquid; the above cycle of changes is then repeated until there appears to be no further absorption. The liquid is finally saturated with acetylene, and is then shaken up with water to remove any chloride of sulphur and distilled with steam. The oily distillate, after washing with sodium carbonate, is fractionally distilled, when a mixture of *s*-tetrachloroethane, pentachloroethane, and hexachloroethane is obtained, the two latter only in small quantity. Hexachloroethane is obtained by alternately passing dry acetylene and dry chlorine into gently boiling disulphur dichloride mixed with from 1 to 2 per cent. of reduced iron and contained in a reflux apparatus. Finally the solution is saturated with chlorine, and, while hot, poured off from a dark, amorphous solid and allowed to cool. A portion of the hexachloroethane hereby crystallises out, and can be purified by sublimation and crystallisation from alcohol; the mother liquors are then put back again and alternately saturated with chlorine and acetylene.

P. H.

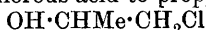
Decomposition of Copper Sulphate by Methyl Alcohol. VICTOR AUGER (*Compt. rend.*, 1906, 142, 1272—1274. Compare Klepl, *Abstr.*, 1882, 1274; de Bruyn, *Abstr.*, 1893, i, 244; de Forcrand, *Abstr.*, 1886, 524).—Hydrated copper sulphate is soluble to the extent of 11.5 per cent. in methyl alcohol at 0°, and the *basic sulphate*, $3CuSO_4 \cdot CuO \cdot 4CH_3O$, separates from the solution in the form of rosettes of small, green needles; this compound, which can be obtained in much larger quantity by the prolonged boiling of a 2.5 per cent. solution of copper sulphate in methyl alcohol, or by shaking anhydrous copper sulphate in contact with methyl alcohol for a week,

is stable in a vacuum over sulphuric acid, but decomposes slowly at 110° or in contact with moist air.

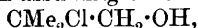
Pickering has shown (*Chem. News*, 1883, 47, 181) that when a 1.28 per cent. aqueous solution of copper sulphate is boiled, 2.5 per cent. of the copper is deposited in the form of the basic salt, $6\text{CuO}\cdot 2\text{SO}_3\cdot 5\text{H}_2\text{O}$, but a methyl alcohol solution of the same dilution deposits 73 per cent. of the copper as the above basic salt.

Methyl alcohol decomposes zinc sulphate, forming a basic salt, and also, but to a much less extent, cobalt or nickel sulphates. Ethyl alcohol is much less active than methyl alcohol in promoting the decomposition of copper sulphate. M. A. W.

Application of the Principle of Partition. IV. Addition of Hypochlorous Acid to *iso*Butylene. ARTHUR MICHAEL and VIRGIL L. LEIGHTON (*Ber.*, 1906, 39, 2157—2163. Compare this vol., i, 550, 559).—Markownikoff first showed that the propylene chlorohydrin, formed by the addition of hypochlorous acid to propylene, has the formula



and not $\text{CHMeCl}\cdot\text{CH}_2\cdot\text{OH}$. The authors now show that Butleroff and Henry are incorrect in assuming that the chlorohydrin,



is formed by the addition of hypochlorous acid to *isobutylene*; the isomeric compound, $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\text{Cl}$, is produced. The rule is submitted that the addition of hypochlorous acid to α -alkylenes leads to the formation of alkylene chlorohydrins, where the chlorine atom is attached to a terminal carbon atom which was previously unsaturated. This is not actually contradictory to the principle of distribution enunciated by one of the authors.

isoButylene chlorohydrin is a colourless oil which boils at 128° (corr.) and has a sp. gr. 1.0663 at 20° . At the ordinary temperature, it is very slowly decomposed by water into hydrochloric acid and *isobutaldehyde*. Its constitution was deduced from its behaviour on dehydration with phosphoric oxide when *chloroisobutylene* was formed. A. McK.

Application of the Principle of Partition. II. Constitution of the Hexyl Alcohol prepared from Mannitol Hexylene. ARTHUR MICHAEL and ROBERT N. HARTMAN (*Ber.*, 1906, 39, 2149—2152. Compare this vol., i, 550).—The product obtained by the addition of water to hexylene from mannitol does not consist of β -hexanol alone, but is a mixture of β -hexanol and γ -hexanol. The product was submitted to gentle oxidation and the constitution of the resulting ketone mixture determined by the semicarbazide method (*loc. cit.*). The conclusion is drawn that the hexanol mixture contains about 77 per cent. of β -hexanol and 23 per cent. of γ -hexanol.

A. McK.

Acetyl Chloride as a Reagent for Pinacolyl Alcohols. MAURICE DELACRE (*Bull. Acad. roy. Belg.*, 1906, 134—139).—Henry's experiments (this vol., i, 329) on the action of acetyl chloride on methyl*tert.*-butylcarbinol and dimethyl*isopropyl*carbinol have been repeated, and in both cases the author obtained, as a principal product, an ester boiling at

135—142°. The dimethylisopropylcarbinol used was prepared by Masson's method (Abstr., 1901, i, 249) and differed slightly in boiling point from that used by Henry.

The author has already shown that in the case of the action of hydrogen bromide on ψ -butylethylene ($\gamma\gamma$ -dimethyl- Δ^2 -butylene) (this vol., i, 476) the course of the reaction is dependent on the purity of the hydrocarbon, and suggests that it will be necessary to repeat Henry's experiments with carefully purified specimens of the two alcohols before his method of differentiating between the *sec.*- and *tert.*-alcohols can be accepted.

T. A. H.

Etherates of Magnesium Bromide and Iodide. II. The Monoetherate of Magnesium Bromide. BORIS N. MENSCHUTKIN (*Zeit. anorg. Chem.*, 1906, 49, 207—212. Compare Abstr., 1904, i, 215; this vol., i, 131, 132).—The solubility relations of ether and the monoetherate of magnesium bromide have been investigated. The saturated solution of the monoetherate in ether is stable between 30° and 158°, the solubility decreasing regularly from 49.1 to 41 per cent. by weight of magnesium bromide between 0° and 158°; below 30°, addition of a trace of dietherate causes the separation of this substance in crystals, whilst above 158° a second liquid layer is formed with separation of monoetherate. When a quantity of etherate corresponding with about 4 per cent. of magnesium bromide is present, the second layer disappears and the solubility curve can be followed to higher temperatures; at 170°, the solution contains only about 0.13 per cent. of magnesium bromide. The solubility curves of ether in the saturated solution of the monoetherate and of the latter solution in ether have also been determined; the systems are stable between 22.8° and 158°.

The complete results obtained in the present and former papers (Abstr., 1904, i, 215) for the equilibrium relations of ether and the mono- and di-etherates are represented diagrammatically.

G. S.

New Synthesis of Methyl Ethyl Xanthate. HARRY S. FRY (*J. Amer. Chem. Soc.*, 1906, 28, 796—798).—When magnesium is allowed to react with a solution of carbon disulphide in methyl alcohol, magnesium methyl xanthate is produced. If the product of the reaction is treated with ethyl bromide and the mixture is afterwards acidified with dilute sulphuric acid, methyl ethyl xanthate, $\text{OMe}\cdot\text{CS}\cdot\text{SEt}$, is obtained in a yield of 62.5 per cent. of the theoretical.

E. G.

Sulphoacetic Acid. OTTO STILLICH (*J. pr. Chem.*, 1906, [ii], 73, 538—544. Compare Abstr., 1905, i, 318).—The yield of sulphoacetic acid, obtained on heating glacial acetic acid with sulphuric acid, depends on the temperature and the amount of water present. The product is isolated as barium sulphoacetate, which, when heated with aniline sulphate in aqueous solution, forms *aniline hydrogen sulphoacetate*; this crystallises in glistening, nacreous leaflets and melts at 187—188°. Contrary to Baumstark's statement (*Annalen*, 1866, 140, 81), the formation of sulphoacetic acid by the interaction of chlorosulphonic and glacial acetic acids commences at 40°, the yield increasing

to about 30 per cent. as the temperature rises to 140° ; above 80° , carbon dioxide and sulphur dioxide are formed. The barium salt is obtained in an 83 per cent. yield by Franchimont's method (Abstr., 1881, 716) or in a 92 per cent. yield by boiling chloroacetic acid with sodium sulphite and sodium carbonate in aqueous solution and precipitating the product with barium chloride.

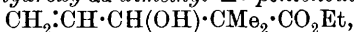
Free sulphoacetic acid is prepared by treating the barium salt with sulphuric acid. It is moderately stable towards concentrated sulphuric acid, commencing to evolve carbon dioxide at 190° and sulphur dioxide only at 210° (compare Carius, *Annalen*, 1862, 124, 55).

Ammonium sulphoacetate, $C_2H_5O_5S(NH_4)_2$, crystallises in needles, melts at $153-173^{\circ}$, is not hygroscopic, and has an acid reaction to litmus. The *strontium* salt, $C_2H_5O_5SSr \cdot H_2O$, formed by adding strontium chloride to the barium salt in aqueous solution, crystallises in pointed needles and loses H_2O at $230-240^{\circ}$. The calcium salt forms small prisms containing $1\frac{1}{6}H_2O$ (compare Franchimont, Abstr., 1888, 1177). G. Y.

Derivatives of Sebacic Acid. FRIEDRICH KRAFFT (*Ber.*, 1906, 39, 2193—2197. Compare Phookan and Krafft, Abstr., 1892, 1180).—Decamethyleneimine hydrochloride is obtained in a 65—70 per cent. yield if the mixture of sodium chloride and decamethylenediamine formed by reduction of sebacamide is heated under 100—120 mm. pressure. The free base, boiling at $100-102^{\circ}$ under 13 mm. pressure, reacts with benzoyl chloride in a freezing mixture, forming *benzoyl-decamethyleneimine*, $\begin{matrix} CH_2 \cdot [CH_2]_3 \cdot CH_2 \\ CH_2 \cdot [CH_2]_3 \cdot CH_2 \end{matrix} > NBz$. This melts at $27.5-28^{\circ}$, boils at 175° in a vacuum, is readily soluble in alcohol or ether, and when oxidised by aqueous potassium permanganate at $35-40^{\circ}$ yields *benzoyl-i-aminodecoic acid*, $NHBz \cdot [CH_2]_9 \cdot CO_2H$, which separates from alcohol or hot water in small, white crystals and melts at 74° . The *barium* salt, $(C_{17}H_{24}O_3N)_2Ba$, is described. When heated in a vacuum, the acid decomposes, forming *i-aminodecoic anhydride*, $C_9H_{18} \begin{matrix} CO \\ \diagup \diagdown \\ NH \end{matrix}$, which solidifies to a white, crystalline mass, melts at $64-66^{\circ}$, and boils at $200-205^{\circ}$ in a vacuum.

The *hydrochloride* of *i-aminodecoic acid* is formed by heating the benzoyl derivative with concentrated hydrochloric acid at $110-120^{\circ}$ in a sealed tube; it forms deliquescent crystals, and when treated with silver oxide yields the free *acid*, $NH_2 \cdot [CH_2]_9 \cdot CO_2H$. This melts and decomposes at 164° , is readily soluble in water, but less so in alcohol, and is insoluble in ether. The *platinichloride*, $(C_{10}H_{21}O_2N)_2 \cdot H_2PtCl_6$, was analysed. G. Y.

Abnormal Dehydration of Hydroxyalkylpivalic Esters. I. EDMOND E. BLAISE and ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, [iii], 35, 360—373. Compare following abstract).—*Ethyl β -hydroxy- β -vinylpivalate* [*β -hydroxy- $\alpha\alpha$ -dimethyl- Δ^{γ} -pentenoate*],



prepared by condensing ethyl bromoisobutyrate with acraldehyde, is a

viscous liquid and boils at 106° under 19 mm. pressure. The *phenylurethane* of the ester is crystalline and melts at 66° . The *free acid* obtained by hydrolysing the ethyl ester with alcoholic potash is viscous, boils at 159° under 23 mm. pressure, and on bromination yields an amorphous *dibromide*. The *calcium* and *barium* salts crystallise with 3 and 5 mols. of water respectively. The *phenylurethane* of the acid crystallises in needles from a mixture of benzene and light petroleum and melts at $90-95^{\circ}$.

When ethyl β -hydroxy- $\alpha\alpha$ -dimethyl- Δ^{γ} -pentenoate is dehydrated with phosphoric oxide in presence of benzene, a mixture of gaseous and liquid hydrocarbons, tetramethylsuccinic acid, and some δ -phenyl- $\alpha\alpha$ -dimethyl- Δ^{β} -pentenoic acid are produced. When the operation is conducted in presence of toluene, a mixture of *o*- and *p*-tolylidimethyl- Δ^{β} -pentenoic acids is formed, whilst in presence of chloroform much gas is evolved and almost complete decomposition ensues. γ -Benzyl- $\alpha\alpha$ -dimethylvinylacetic acid [δ -phenyl- $\alpha\alpha$ -dimethyl- Δ^{β} -pentenoic acid],



best purified through its *calcium* salt, is a viscous liquid and boils at 195° under 20 mm. pressure, and on bromination yields an oily unstable *dibromide*. The *methyl* ester, best obtained by the interaction of the acid chloride with methyl alcohol, is liquid and boils at 154° under 17 mm. pressure. The *ethyl* ester, similarly prepared, boils at 154° under 12 mm. pressure. The *acid chloride* is a liquid with a disagreeable, irritating odour, and boils at $158-159^{\circ}$ under 20 mm. pressure. The *amide* crystallises from ether in silky spangles and melts at $104-105^{\circ}$; the *anilide* separates from a mixture of ether and light petroleum in long prisms and melts at 90° , and the *phenylhydrazide* is crystalline and melts at 99° . β -Hydroxy- δ -phenyl- $\alpha\alpha$ -

dimethyl- γ -valerolactone,
$$\begin{array}{c} \text{OH}\cdot\text{CH}-\text{CMe}_2 \\ | \\ \text{CH}_2\text{Ph}\cdot\text{CH}-\text{O} \end{array} \text{CO},$$
 is obtained by careful oxidation of δ -phenyl- $\alpha\alpha$ -dimethyl- Δ^{β} -pentenoic acid with potassium permanganate. It crystallises from a mixture of benzene and light petroleum and melts at 100° . The final oxidation products of δ -phenyl- $\alpha\alpha$ -dimethyl- Δ^{β} -pentenoic acid are dimethylmalonic and benzoic acids, the latter being probably formed from phenylacetic acid.

The δ -tolyl- $\alpha\alpha$ -dimethyl- Δ^{β} -pentenoic acid, obtained on dehydrating ethyl hydroxydimethylpentenoate in presence of toluene, is a viscous liquid and boils at 199° under 16 mm. pressure, and must consist of a mixture of the ortho- and para-derivatives, since on oxidation with permanganate it yields a mixture of terephthalic and *p*- and *o*-toluic acids. The other oxidation products are *o*- and *p*-tolualdehyde, identified by their *semicarbazones*, which melt respectively at 212° and 234° , and dimethylmalonic acid. It is pointed out that *p*-toluic acid is not, as is generally stated, readily soluble in warm water or steam.

T. A. H.

Dehydration of β -Hydroxy- β -alkylpivalic Esters. Parts III and IV. ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, [iii], 35, 298—305, 355—360. Compare this vol., i, 230, 396).—Ethyl β -hydroxy- $\beta\beta$ -dimethylpivalate [β -hydroxy- $\alpha\alpha\beta$ -trimethylbutyrate],

$\text{OH}\cdot\text{CMe}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$, prepared by condensing acetone with ethyl bromoisobutyrate, boils at 91° under 17 mm. pressure (compare Reformatsky and Plesconossoff, Abstr., 1896, i, 128). The *acetyl* derivative is a viscous liquid and boils at 119° under 23 mm. pressure. When dehydrated with phosphoric oxide in the usual way (*loc. cit.*), the ester yields *ethyl $\alpha\alpha$ -dimethylisopropenylacetate* [$\alpha\alpha\beta$ -trimethyl- $\Delta\beta$ -butenoate], $\text{CH}_2\cdot\text{CMe}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$. This is a mobile liquid of pleasant odour and boils at 161° . The *methyl* ester is similar and boils at 148° . The *free acid*, obtained with difficulty by hydrolysing the ethyl ester with alcoholic potash, is crystalline, melts at 35° , boils at 117° under 28 mm. pressure, and is very hygroscopic. The hydrated *calcium*, *barium*, and *lead* salts are crystalline. The *chloride* is a mobile liquid with a sharp disagreeable odour and boils at 60° under 30 mm. pressure. The *amide* crystallises from ether in pearly lamellæ and melts at 107 – 108° , the *anilide* forms needles from a mixture of ether and light petroleum and melts at 61° ; the *phenylhydrazide* crystallises from boiling alcohol and melts at 141° ; and the β -*naphthylamide* separates from boiling alcohol in small needles and melts at 94° .

$\beta\gamma$ -Dibromo- $\alpha\alpha\beta$ -trimethylbutyric acid, $\text{CH}_2\text{Br}\cdot\text{CMeBr}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$, prepared by brominating $\alpha\alpha\beta$ -trimethylbutenoic acid in carbon disulphide at 0° , crystallises from a mixture of ether and light petroleum and melts at 125 – 126° . The *methyl* ester is liquid and boils at 130° under 10 mm. pressure.

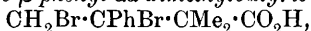
On reduction with sodium, ethyl trimethylbutenoate yields the corresponding $\beta\beta\gamma$ -trimethyl- $\Delta\gamma$ -butenol, $\text{CH}_2\cdot\text{CMe}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$. This is a mobile liquid of slight odour and boils at 152° . The *acetate* has a pleasant odour and boils at 170 – 171° , and the *phenylurethane* forms splendid needles from light petroleum and melts at 73° .

When oxidised with permanganate, trimethylbutenoic acid furnishes methyl isopropyl ketone, trimethylmalic acid, which melts and decomposes at 200 – 210° (compare Auwers and Campenhausen, Abstr., 1896, i, 424, and Komppa, *ibid.*, i, 597), and β -hydroxy- $\alpha\alpha\beta$ -trimethylbutyrolactone, $\begin{array}{c} \text{OH}\cdot\text{CMe}\cdot\text{CMe}_2 \\ | \\ \text{CH}_2-\text{O} \end{array} > \text{CO}$, which crystallises from dry ether and melts at 103° .

Ethyl β -hydroxy- β -phenyl- β -methylpivalate [β -hydroxy- β -phenyl- $\alpha\alpha$ -dimethylbutyrate], prepared by condensing acetophenone with ethyl bromoisobutyrate, is a syrupy liquid, boils at 154° under 10 mm. pressure, and on treatment with dilute alcoholic potash yields acetophenone and isobutyric acid. Some dypnone is produced as a by-product in the primary condensation: *dypnone semicarbazone* crystallises from benzene and melts at 151° . When ethyl β -hydroxy- β -phenyl- $\alpha\alpha$ -dimethylbutyrate is dehydrated with phosphoric oxide it yields *ethyl phenyldimethylvinylacetate* [β -phenyl- $\alpha\alpha$ -dimethyl- $\Delta\beta$ -butenoate], $\text{CH}_2\cdot\text{CPh}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$. This is a liquid and boils at 132° under 10 mm. pressure. The *methyl* ester boils at 133° under 19 mm. pressure. The *free acid* is a syrup and boils at 167° under 8 mm. pressure. The *potassium*, *calcium*, and *lead* salts are crystalline. The *chloride* is a mobile liquid of disagreeable odour and boils at 130° under 13 mm. pressure. The *amide* crystallises from ether and melts at 118° , the *anilide* separates from alcohol in needles and melts at

85°, and the *phenylhydrazide* forms lamellæ from alcohol and melts at 159°.

On bromination in carbon disulphide at 0°, phenyldimethylbutenoic acid yields *βγ-dibromo-β-phenyl-αα-dimethylbutyric acid*,



which crystallises from benzene and melts and decomposes at 165°.

When phenyldimethylbutenoyl chloride is treated with zinc methyl, *β-phenyl-αα-dimethyl-β-allyl methyl ketone*, $\text{CH}_3\cdot\text{CPh}\cdot\text{CMe}_2\cdot\text{COMe}$, is produced. It is a pleasant-smelling liquid, which boils at 123° under 10 mm. pressure. The *semicarbazone* crystallises from alcohol and melts at 192°.

γ-Phenyl-ββ-dimethyl-Δ⁴-butenol, $\text{CH}_3\cdot\text{CPh}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$, obtained by reducing ethyl phenyldimethylbutenoate with sodium, is a sweet-smelling, syrupy liquid, which boils at 141° under 17 mm. pressure and is not volatile in steam. The *acetate* boils at 145° under 15 mm. pressure.

T. A. H.

Xanthophanic and Glaucophanic Acids. CARL LIEBERMANN (*Ber.*, 1906, 39, 2071—2088).—Claisen's xanthophanic and glaucophanic acids (*Abstr.*, 1897, i, 594) are shown by Zeisel's method to contain respectively two and approximately three ethoxyl groups, and should therefore, the author considers, be called ethyl xanthophanic and ethylglaucophanic acids [xanthophanic acid ethyl ether and glaucophanic acid ethyl ether]. From the chloroform or benzene mother liquor of the crude xanthophanic acid ethyl ether (*loc. cit.*), a *substance*, $\text{C}_{20}\text{H}_{22}\text{O}_5$, is obtained, which crystallises rapidly from alcohol or light petroleum in colourless, glassy needles, contains two ethoxyl groups, melts at 97°, and is very similar to Claisen's ethyl methenylbisacetate, but differs from it by its insolubility in alkalis; the *bromophenylhydrazone*, $\text{C}_{26}\text{H}_{27}\text{O}_4\text{N}_2\text{Br}$, crystallises in yellow needles and melts at 178°. After the estimation of ethoxyl in this by-product, the de-alkylated residue is obtained from alcohol in colourless needles which melt at 265° and, after sublimation, at 280°; it has an acid reaction and does not give a coloration with ferric chloride.

Xanthophanic acid and glaucophanic acid methyl ethers are obtained in better yield than the corresponding ethyl compounds when methyl methoxymethyleneacetoacetate (2 mols.) and methylsodioacetoacetate (1 mol.) are melted together on the water-bath. The *xanthophanic acid methyl ether*, $\text{C}_{16}\text{H}_{16}\text{O}_8$, is separated from the accompanying sodium glaucophanate methyl ether by solution in chloroform. It separates from benzene in red needles and melts at 179°; from the mother liquor, dark blue metallic prisms are obtained, having the same composition and melting point. *Sodium glaucophanate methyl ether*, $\text{C}_{24}\text{H}_{19}\text{O}_{12}\text{Na}$, forms greenish-blue crystals insoluble in chloroform. The *acid*, $\text{C}_{24}\text{H}_{20}\text{O}_{12}$, melts and decomposes at 206°. The by-product in the reaction is a *substance*, $\text{C}_{18}\text{H}_{18}\text{O}_5$, which separates from light petroleum in colourless needles, melts at 133°, is insoluble in alkalis, and contains methoxyl; the de-methylated residue is a colourless acid, melts at 260°, and sublimes in colourless needles.

Sodium methoxide and xanthophanic acid ethyl ether react in benzene solution to form a *substance* which separates from benzene

in colourless crystals, melts at 143° , dissolves in alkalis, and gives a red coloration with ferric chloride. Xanthophanic acid methyl ether and glaucophanic acid ethyl and methyl ethers form analogous compounds.

Magnesium methoxide reacts with xanthophanic acid ethyl ether to form a *substance* which crystallises in yellow needles and melts at $160\text{--}161^{\circ}$. With glaucophanic acid ethyl ether, magnesium methoxide reacts to form two substances: the one is sparingly soluble in benzene and acetic acid and melts at 213° , the other dissolves readily and melts at 199° ; both crystallise in yellow needles and are soluble in a cold solution of sodium carbonate.

Magnesium methoxide and xanthophanic acid methyl ether form a *substance* which crystallises in yellow needles, melts and decomposes at 162° , and forms a *bromophenylhydrazone* melting at 224° . The substance obtained by the action of magnesium methoxide on xanthophanic acid methyl or ethyl ether or on glaucophanic acid ethyl ether is decomposed by a concentrated solution of potassium hydroxide, forming an *acid* which crystallises in white needles, melts and decomposes at 255° , gives a red coloration with ferric chloride, and yields resacetophenone on sublimation; the same acid can be directly obtained from xanthophanic acid ethyl or methyl ether.

Xanthophanic acid ethyl ether reacts with semicarbazide hydrochloride in the presence of methyl alcohol and sodium acetate to form *hydrazodicarbonamide*, $(\text{NH}_2\cdot\text{CO}\cdot\text{NH})_2$, which crystallises in colourless needles and melts at 253° , and a *substance*, $\text{C}_{19}\text{H}_{23}\text{O}_8\text{N}_3$, which melts at 194° , does not regenerate xanthophanic acid by treatment with hydrochloric acid, and does not show the following characteristic test for the acid. When xanthophanic acid methyl or ethyl ether is warmed with concentrated sulphuric acid, the red colour of the solution suddenly disappears and a yellow, fluorescent solution is obtained, from which can be isolated a *substance*, $\text{C}_{14}\text{H}_{10}\text{O}_7$, which crystallises in golden scales, melts and decomposes at 185° , dissolves in alkali without fluorescence, and forms a brominated derivative melting and decomposing at $270\text{--}275^{\circ}$.

When sodium glaucophanate ethyl or methyl ether is warmed with dilute nitric acid, a *substance* is obtained which does not contain nitrogen, crystallises in yellow needles, becomes brown at 170° , melts at 194° , and contains ethoxyl. C. S.

Decomposition of the Oxalates of the Alkaline Earths by Aqueous Solutions of Alkali Sulphates. H. CANTONI (*Arch. Sci. phys. nat.*, 1906, [iv], 21, 469—494).—Solutions of alkali sulphates were added to the oxalates of the alkaline earths, and the quantity of the oxalate which passed into solution estimated by permanganate. Complete tables of the results are given. In general, potassium sulphate has a greater effect than the sulphates of sodium or ammonium, and the decomposition of the oxalate is greatest for the barium salt and least for the calcium salt. This is what would be expected from the relative solubilities. Thus, in the case of a $4/25N$ solution of potassium sulphate after nine hours, the decomposition by the oxalate of barium reached 50 per cent., by oxalate of strontium 6.88 per cent., and by calcium oxalate 0 per cent. L. M. J.

Preparation of Adipic Acid. ERIK ROSENLEW (*Ber.*, 1906, 39, 2202. Compare Mannich, this vol., i, 432).—The conditions are detailed under which adipic acid is obtained in a 70—75 per cent. yield, by the oxidation of *cyclohexanone* by means of potassium permanganate in sodium carbonate solution. G. Y.

Antimony Tartrate and its Ethyl Ester. J. BOUGAULT (*J. Pharm. Chim.*, 1906, [vi], 23, 465—469).—Antimonious oxide is dissolved in an aqueous solution of tartaric acid, and the liquid allowed to evaporate spontaneously to a syrup. On the addition of acetone, a precipitate is formed which rapidly becomes crystalline, and consists of the tartrate, $\text{SbC}_4\text{H}_3\text{O}_6$ (this vol., i, 336), containing 1 mol. of acetone, which it loses at 100° . When the anhydrous tartrate is dissolved in a solution of tartaric acid in alcohol, an *ethyl* ester, $\text{SbC}_4\text{H}_2\text{O}_6\text{Et}$, slowly separates in small, slender needles. This is dissociated by water with the partial precipitation of antimonious oxide. When dissolved in a solution of potassium hydrogen carbonate, some antimonious oxide is precipitated, but this redissolves on boiling, forming tartar emetic. An aqueous solution of potassium tartrate dissolves the ester, giving potassium ethyl tartrate and tartar emetic. T. A. H.

Methylene Compounds. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1906, 206—226).—The first portion of this memoir is devoted to the discussion of De Sonay's work (*ibid.*, 1893, 26, 629, and 1894, 28, 102) on the chlorination of methyl ether and methylal in the light of the new results obtained by Descudé (see following abstract), and it is pointed out that De Sonay's dichloromethylal probably had the formula $\text{CCl}_2(\text{OMe})_2$ in place of $\text{CH}_2(\text{O}\cdot\text{CH}_2\text{Cl})_2$ as he supposed. This correction of De Sonay's work indicates that the chlorination of methylal proceeds normally, the hydrogen atom of the methylene group being replaced before those of the methyl groups.

In the second portion of the memoir, a number of analogies between derivatives of "oxymethylene" and the oxides of the heavy metals are pointed out and illustrated by examples, thus: the compound $(\text{CH}_2)_3\text{O}_2\text{Cl}_2$ is regarded as similar in constitution to the mineral mendipite, $\text{Pb}_3\text{O}_2\text{Cl}$.

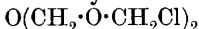
In the third section, it is pointed out that ethylidene compounds (methyl derivatives of methylene) may be regarded as forming a series parallel to that of the methylene compounds.

In connection with the order of replacement of hydrogen atoms by chlorine in substances of these types, it is noted that the action of hydrogen chloride on a mixture of acetaldehyde and alcohol gives rise first to the compound $\text{CHMeCl}\cdot\text{OEt}$, and eventually to $\text{CH}_2\text{Cl}\cdot\text{CHCl}\cdot\text{OEt}$, a reaction which appears to be analogous to the production of $\text{CH}_2\text{Cl}\cdot\text{O}\cdot\text{CH}_2\text{Cl}$ from $\text{CH}_2\text{Cl}\cdot\text{OMe}$, the chlorine in both cases replacing a hydrogen atom in an unattacked methyl group in preference to entering a group in which substitution has already occurred (compare Littirsch, *Abstr.*, 1904, i, 364). T. A. H.

Order of Substitution of Hydrogen by Chlorine in Methylal. MARCEL DESCUDÉ (*Bull. Acad. roy. Belg.*, 1906, 198—205).—In addition to the dichloromethyl oxide (*Abstr.*, 1904, i, 546), pro-

duced when trioxymethylene is treated with phosphorus trichloride in the presence of zinc chloride, there is formed some *dichloromethylal*, $\text{CH}_2(\text{O}\cdot\text{CH}_2\text{Cl})_2$. This boils at $65-67^\circ$ under 15 mm. pressure, and with slight decomposition at 166° under atmospheric pressure. It has sp. gr. 1.352 at $11^\circ/11^\circ$, and is decomposed immediately by water, yielding hydrogen chloride and formaldehyde, and by alcohols forming water, hydrogen chloride, and monochloromethyl oxide.

When dichloromethyl oxide is heated with trioxymethylene in a closed tube, some dichloromethylal is formed, but the principal reaction is more complex, a *product* which may have the formula



being formed. This is liquid and boils at $100-102^\circ$ under 15 mm. pressure.

The author points out that the several chlorine derivatives of methylal described by De Sonay (*Bull. Acad. roy. Belg.*, 1893, 26, 647) probably exist, but the boiling points ascribed to them by this author indicate that the constitutions he assigned to them are probably erroneous.

T. A. H.

Depression of the Temperature of Reaction in Syntheses with Organic Chloro-compounds. ALFRED WOHL (*Ber.*, 1906, 39, 1951—1954. Compare Hesse, this vol., i, 375).—The action of β -chloropropaldehyde diethylacetal on potassium cyanide (Wohl, Schäfer, and Thiele, this vol., i, 105) and on ethyl sodiocyanoacetate, of alcoholic ammonia on chloroacetaldehyde diethylacetal and on *p*-chloro- and *o*-chloro-nitrobenzenes, of ethyl chloride on potassium phenoxide, of benzotrichloride on sodium amyloxide, and of *as*-dichloroacetone on sodium acetate take place at lower temperatures and with increased yields if 1/10—1/5 mol. of potassium iodide is added for each atom of chlorine entering into the reaction. The corresponding organic iodo-compound is formed as an intermediate product, the alkali iodide being regenerated in the second stage of the reaction.

Reactions which take place readily, such as that of sodium methoxide on *p*- and on *o*-chloronitrobenzene, are not affected by addition of an alkali iodide.

G. Y.

Application of the Principle of Partition. I. Course of the Addition of Water to β -Hexinene. ARTHUR MICHAEL (*Ber.*, 1906, 39, 2143—2148. Compare this vol., i, 550).—The application of the principle of partition enunciated by the author is discussed in the case of the formation of a hexanone by the action of sulphuric acid on Δ^2 -hexinene.

γ -Hexanone, prepared by the action of an ethereal solution of zinc ethyl on propionyl chloride, boils at $123-123.5^\circ$ under 765 mm. pressure.

Attempts to separate β -hexanone from γ -hexanone by means of sodium hydrogen sulphite are described. In a mixture of β -hexanone and γ -hexanone, the amount of each may be estimated, since the former forms a semicarbazone with hydrogen semicarbazide phosphate and the latter does not.

The ketone mixture, formed by the action of sulphuric acid on

Δ^{β} -hexinene, was fractionated, and the ratio of β -hexanone to γ -hexanone in each individual fraction was estimated by means of the semicarbazide method described.

A. McK.

Melezitose and Turanose. GEORGES TANRET (*Compt. rend.*, 1906, 142, 1424—1426. Compare Berthelot, Abstr., 1877, i, 451; Villiers, *ibid.*; Alechin, Abstr., 1886, 683; 1890, 733; Markownikoff, Abstr., 1885, 943).—Melezitose is hydrolysed by heating with 20 per cent. acetic acid solution, yielding turanose and dextrose; after destroying the dextrose by means of yeast, the turanose can be isolated from an alcoholic extract of the residue in the form of transparent, non-crystalline, rounded grains which contain alcohol, have the composition $C_{12}H_{22}O_{11} \cdot \frac{1}{2}C_2H_6O$, melt at 60—65°, and lose their alcohol at 100°, yielding the pure sugar, which has $[\alpha]_D + 71.8^\circ$, does not exhibit mutarotation, and has a reducing power of 60, that of dextrose being taken as 100.

Turanose is not attacked by the ordinary soluble ferments, such as emulsin or diastase; but is readily hydrolysed by mineral acids, yielding an equal molecular mixture of dextrose and lævulose, and not dextrose only as stated by Alechin (Abstr., 1890, 733).

M. A. W.

Behaviour of Starch on Hydrolysis with Moderately Concentrated Sulphuric Acid. BERNHARD TOLLENS (*Ber.*, 1906, 39, 2190—2193).—The product of the hydrolysis of potato starch with 8 per cent. sulphuric acid contains dextrose, at most only traces of mannose, and no galactose. The author concludes that the mannose and galactose obtained on hydrolysis of reindeer mosses (Ulander and Tollens, this vol., ii, 193) were derived from the hemicelluloses of the lichens and not from glucoses.

G. Y.

Cellulose Acetates. HERMANN OST (*Zeit. angew. Chem.*, 1906, 19, 993—1000).—The author is of opinion that all the acetates of cellulose described by previous authors are in reality triacetates of substances derived from the hydrolysis of ordinary cellulose.

P. H.

Copper Alkali Cellulose. WILHELM NORMANN (*Chem. Zeit.*, 1906, 30, 584—585).—When cotton wool is treated with a solution of copper hydroxide in sodium hydroxide, it swells up and is converted into a stable copper alkali cellulose, which on analysis is found to contain cellulose and copper oxide in the ratio $C_{12}H_{20}O_{10} : CuO$. The same substance may also be obtained in the form of clear, glassy threads by allowing a fine stream of copper ammonia cellulose to flow into a solution of an alkali hydroxide.

P. H.

New Syntheses of Amines by means of Finely-divided Nickel. ALPHONSE MAILHE (*Chem. Zeit.*, 1906, 30, 458—459. Compare Abstr., 1905, i, 401, 501).—Nitriles, when reduced by hydrogen in the presence of finely-divided nickel or copper, yield a mixture of primary, secondary, and tertiary amines and ammonia, the reaction probably taking place as follows: (i) $RCN + 2H_2 = RCH_2 \cdot NH_2$;

(ii) $2\text{RCH}_2\cdot\text{NH}_2 = \text{NH}(\text{CH}_2\text{R})_2 + \text{NH}_3$; and (iii) $3\text{RCH}_2\cdot\text{NH}_2 = \text{N}(\text{CH}_2\text{R})_3 + 2\text{NH}_3$. In the case of benzonitrile, the corresponding amines are only formed with copper, nickel giving toluene. Aldoximes or ketoximes similarly give rise to a mixture of primary, secondary, and tertiary amines, but only a very small amount of the latter; the method is a very convenient one for preparing secondary amines of the type $\text{NH}(\text{CR}^1\text{R}^2)_2$. Acid amides, except formamide, likewise yield primary and secondary amines. When nickel is employed as the catalyst, the temperature must not be allowed to exceed 220° , but with copper the temperature may be anywhere between 200° and 300° . P. H.

Resolution of α -Aminoisovaleric Acid into its Optically Active Components. EMIL FISCHER, KOICHI MATSUBARA, and SIEGFRIED HILPERT (*Ber.*, 1906, 39, 2320—2328).—The names “valin” and “valyl” are proposed for α -aminoisovaleric acid and the group $\text{CHMe}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}$ respectively.

Formyl-i-valin, $\text{C}_6\text{H}_{11}\text{O}_3\text{N}$, obtained from *i*-valin like formyl-leucine (this vol., i, 72), separates from hot water in large, rhombic plates, has an acid taste, is easily soluble in alkalis and ammonia, sinters at 137° , and melts at 140 — 145° (corr.). After treating the hot methyl alcoholic solution with brucine, the salt of *formyl-l-valin* separates from the cold liquid in small needles, while the brucine salt of *formyl-d-valin* is obtained by evaporating the alcoholic mother liquor. The formyl derivatives, liberated by a slight excess of normal sodium hydroxide, separate from hot water in small prisms, sinter at 150° , and melt at 156° (corr.); formyl-*l*-valin has $[\alpha]_D$ at 20° , -13° in alcoholic and 16.9° in aqueous solution, and formyl-*d*-valin has $[\alpha]_D$ 13.05° at 20° in alcoholic solution.

By hydrolysis with 10 per cent. hydrobromic acid, *d*-valin and *l*-valin are obtained in colourless, microscopic, six-sided leaflets. The former melts in a sealed tube at 315° (corr.), sublimes with partial anhydride formation when strongly heated, has a somewhat sweet and bitter taste, and at 20° in 20 per cent. hydrochloric acid has $[\alpha]_D$ 28.75° , and in water 6.42° . *l*-Valin has a sweeter taste than its isomeride, and in 20 per cent. hydrochloric acid has $[\alpha]_D$ -28.72° at 20° .

d-Valinphenylcarbimide (compare Schulze and Winterstein, *Abstr.*, 1902, i, 595) softens at 140° , melts and partially decomposes at 147° (corr.), and by rapid boiling with 20 per cent. hydrochloric acid yields *d*-phenylisopropylhydantoin, which melts at 131 — 133° (corr.) (124° , Schulze and Winterstein, *loc. cit.*), and has $[\alpha]_D$ -97.5° at 20° in alcoholic solution.

l-Valinphenylcarbimide has $[\alpha]_D$ -19.02° at 20° .

l-Phenylisopropylhydantoin melts at 131 — 133° (corr.) and has $[\alpha]_D$ 97.22° at 20° in alcoholic solution. C. S.

Salts of Heavy Metals with Feeble Acids and attempts to prepare Colloidal Metallic Oxides. HEINRICH LEY and FRITZ WERNER (*Ber.*, 1906, 39, 2177—2180. Compare Ley, *Abstr.*, 1905, ii, 524; Paal and Leuze, this vol., ii, 356, 358).—Coppersuccinimide

is readily prepared by the addition of sodium hydroxide, drop by drop, to a warm aqueous solution of copper acetate and succinimide. *Cobaltsuccinimide*, $(C_4H_4O_2N)_2Co, 6H_2O$, formed in the same way from cobalt acetate, is obtained as a salmon-coloured, crystalline precipitate, dissolves in alcohol forming a violet solution, and is hydrolysed on addition of water. *Nickelsuccinimide*, $(C_4H_4O_2N)_2Ni, 8H_2O$, prepared from nickel acetate, forms light blue crystals, melts at $110-111^\circ$, and is more stable than the preceding salts towards water, forming a green, very dilute aqueous solution at about 30° ; when heated this becomes suddenly blue and opalescent, in which state it is stable in absence of air, the nickel hydroxide is thrown down by addition of salts, and the succinimide can be removed partially by hydrolysis.

Camphorimide, like succinimide, is a feeble acid. The *copper sodium* salt, $(C_{10}H_{14}O_2N)_2Cu, 2C_{10}H_{14}O_2NNa, 10H_2O$, is formed by the action of copper acetate on the sodium derivative in concentrated aqueous solution; it forms reddish-violet leaflets and yields blue copper hydroxide when treated with cold water, or a brown hydrated oxide when heated with water. The copper sodium salt is decomposed by acetic acid, camphorimide being formed. G. Y.

Decomposition of Hydroxylamine in Presence of Hydrogen Ferrocyanide: Formation of Crystalline Ferrocyanide-violet and Nitroprusside. KARL A. HOFMANN and H. ARNOLDI (*Ber.*, 1906, 39, 2204—2208. Compare Hofmann, *Abstr.*, 1905, i, 512; Tanatar, *Abstr.*, 1902, ii, 386).—When boiled with an equal weight of potassium ferrocyanide in aqueous solution, hydroxylamine hydrochloride yields ammonium chloride, potassium nitroprusside, hydrogen cyanide, nitrogen, and *ferric ammonium ferrocyanide*, $Fe'''[(FeC_6N_6)NH_4]_2$, which separates as a deep blue, crystalline powder with purple lustre. It is formed also when hydroxylamine hydrochloride is boiled with potassium ferrocyanide in aqueous solution. In its properties, it resembles Williamson's violet. It remains unchanged when treated with water, dilute mineral acids, aqueous oxalic acid, glacial acetic acid, sodium potassium tartrate, or ferric chloride solution, or when boiled with 5 per cent. aqueous potassium hydroxide. The colour remains unchanged when the crystalline violet is digested with hydrogen sulphide solution. Ferric hydroxide is formed only slowly when the salt is digested with 4 per cent. ammonia at the ordinary temperature.

The quantitative examination of the reaction between hydroxylamine and potassium ferrocyanide shows that one-half of the latter forms the nitroprusside, whilst the other is converted into the ferric ammonium ferrocyanide. The hydrogen cyanide formed, which corresponds with one-quarter of the total ferrocyanide, does not enter into reaction with the hydroxylamine, whilst sodium nitroprusside and hydroxylamine hydrochloride form a dull blue powder only on prolonged boiling in aqueous solution. G. Y.

Reduction of Blue Iron-cyanogen Compounds. MORITZ KOHN (*Zeit. anorg. Chem.*, 1906, 49, 443—444).—Prussian blue and Turnbull's blue can be conveniently and rapidly reduced by the action of a concentrated sodium hydrogen sulphite solution containing a little

stannous chloride. The author considers that the reducing action is due to hyposulphurous acid produced by the action of stannous chloride. The statement in the literature, that sulphurous acid is reduced to hydrogen sulphide by stannous chloride, is only true if the latter reagent is present in excess. G. S.

Silicones. OCTAVE BOUDOUARD (*Compt. rend.*, 1906, 142, 1528—1530).—The grey, amorphous residues, obtained by treating silicon steels containing 0.9 to 5.1 per cent. of silicon with hydrochloric acid until the iron is completely dissolved, have been analysed by Friedel and Ladenburg's method and also by the combustion method. The analytical data indicate that the silicones present in the residues, which evolve hydrogen when treated with alkali hydroxides, are mixtures, in variable proportions, of silicoformic anhydride and silico-oxalic acid. The residue obtained from an iron silicide, prepared by the thermite process and containing 10 per cent. of silicon, gave similar analytical numbers. H. M. D.

Ethyl Mercuri-*aci*-nitroacetate Anhydride. ROLAND SCHOLL and B. NYBERG (*Ber.*, 1906, 39, 1956—1959. Compare Scholl and Schöfer, *Abstr.*, 1901, i, 359; Hantzsch and Auld, this vol., i, 471).—*Ethyl mercuri-aci-nitroacetate anhydride*, $\text{O} \begin{array}{c} \text{NO} \\ \diagup \quad \diagdown \\ \text{Hg} \end{array} \text{C} \cdot \text{CO}_2\text{Et}$, is formed as a white, crystalline precipitate when mercuric chloride is added to a concentrated aqueous solution of ethyl ammonium *aci*-nitroacetate; it sublimes when carefully heated, detonates when strongly heated, and on ignition burns rapidly with a luminous flame. It is almost insoluble in boiling water, but dissolves readily in dilute sodium hydroxide, ammonia, or hydrochloric acid, and is not changed by potassium iodide solution. Mercuric sulphide is precipitated by hydrogen sulphide from the ammoniacal solution, whilst the hydrochloric acid solution yields mercurous chloride when boiled with phosphorous acid. The action of bromine in potassium bromide solution on the aqueous suspension leads to the formation of *ethyl dibromonitroacetate*, $\text{NO}_2 \cdot \text{CBr}_2 \cdot \text{CO}_2\text{Et}$, which is obtained as a colourless liquid boiling at 105° under 11 mm. pressure.

Mercuriethylethyl chloride (Meyer, this Journal, 1874, 27, 365, 677) has the constitution $\text{NO}_2 \cdot \text{CHMe} \cdot \text{HgCl}$, as it dissolves in dilute sodium hydroxide, and when treated with aqueous potassium iodide yields the yellow *iodide*, $\text{NO}_2 \cdot \text{CHMe} \cdot \text{HgI}$, which is soluble in an excess of potassium iodide. G. Y.

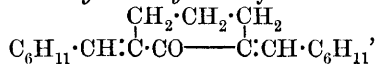
Terpenes and Ethereal Oils. LXXXI. The Simplest Menthene Hydrocarbons of Various Ring Systems and their Conversion into Alicyclic Aldehydes. OTTO WALLACH (*Annalen*, 1906, 347, 316—346. Compare this vol., i, 175, 194, 370).—*cyclopenteneacetic acid* (Wallach and Speranski, *Abstr.*, 1902, i, 800) is now found to melt at 51 — 52° ; when slowly distilled it decomposes, forming *methylenecyclopentane*, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{C} : \text{CH}_2$, which has a pene-

trating odour of leeks, boils at 78—81°, and has a sp. gr. 0.78 and n_D 1.4355 at 19°. On oxidation with 1 per cent. potassium permanganate solution at 0°, it forms the *glycol*, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$, together with pentanone. The *glycol* melts at 39—41°, is readily soluble in all solvents, and when boiled with dilute sulphuric acid loses water, forming *cyclopentanealdehyde*, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{CH} \cdot \text{COH}$. This is obtained as an oil which has an odour like valeraldehyde, distils in a current of steam, and forms a *semicarbazone*, $\text{C}_7\text{H}_{13}\text{ON}_3$, crystallising in leaflets and melting at 123—124°. The *nitrosochloride* of methylenecyclopentane, $(\text{C}_5\text{H}_9\text{ONCl})_2$, decomposes at 80—81°, and reacts with piperidine in alcoholic solution, forming the *nitrolamine*, $\text{C}_6\text{H}_{10}(\text{NO}) \cdot \text{C}_5\text{H}_{10}\text{N}$, which crystallises from alcohol and melts at 116—117°. The action of sodium methoxide on the nitrosochloride leads to the formation of a viscid, unsaturated *oxime*, $\text{C}_6\text{H}_8 \cdot \text{NOH}$, which, on hydrolysis with dilute sulphuric acid, yields *cyclopentenealdehyde* (v. Baeyer and v. Liebig, Abstr., 1898, i, 638).

[With EDUARD ISAAC.]—Ethyl *cyclohexanolacetate* is prepared best by the action of ethyl bromoacetate on *cyclohexanone* in benzene solution in presence of zinc. The *acid*, $\text{CH}_2 < \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, crystallises from a mixture of benzene and light petroleum and melts at 62—64°.

Methylenecyclohexane (Einhorn and Brandtl, Abstr., 1898, i, 407, 433; Sabatier and Mailhe, Abstr., 1904, i, 666, 809), formed by heating *cyclohexeneacetic acid*, boils at 105—106°, has a sp. gr. 0.8025 and n_D 1.4501, and closely resembles Δ^1 -methylcyclohexene (Abstr., 1902, i, 750, 806). When oxidised with potassium permanganate, it forms the *glycol*, $\text{CH}_2 < \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$, and *cyclohexanone*.

The *glycol* forms large crystals, is stable towards air in the absence of acid vapours, and melts at 76—77°. Hexahydrobenzaldehyde (Bouveault, Abstr., 1904, i, 61; Sabatier and Mailhe, *loc. cit.*) is formed by heating the *glycol* with dilute acids. It is obtained as an oil which is soluble in water, polymerises readily, boils at 161—163° under the ordinary pressure, and has a sp. gr. 0.9263 and n_D 1.4495 at 19°. The *semicarbazone* melts at 167—168° (176°; Bouveault, *loc. cit.*). The aldehyde condenses with *cyclohexanone* in alcoholic sodium hydroxide solution, forming *dihexahydrobenzylidenecyclohexanone*,



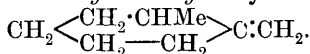
which crystallises in slender needles and melts at 89—90°. With phenylhydrazine, the aldehyde condenses, developing heat and forming a *substance* which crystallises in transparent, red prisms and decomposes on exposure to air. The action of ammonia on the aldehyde in ethereal solution leads to the formation of a *product*, $\text{C}_7\text{H}_{13}\text{N}$, which crystallises in transparent prisms and decomposes at 104—105°.

The *polymeride* of hexahydrobenzaldehyde, $(\text{C}_7\text{H}_{12}\text{O})_2$, is obtained as a colourless oil, which has only a slight odour, and boils at 150—155°

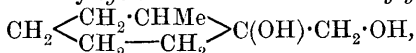
under 11 mm. pressure. A crystalline *polymeride*, $(C_7H_{12}O)_n$, is formed by the action of sulphuric acid on the aldehyde; it crystallises from ethyl acetate in needles and melts at 195—196° or, after resolidifying, at 202—203°.

The *nitrosochloride* of methylenecyclohexane, $(C_7H_{12}ONCl)_2$, reacts with piperidine forming the crystalline *nitrolamine*, $C_7H_{12}(NO) \cdot C_5H_{10}N$, which melts at 127°. Elimination of hydrogen chloride from the nitrosochloride leads to the formation of a viscid *oxime*, $C_7H_{10}:NOH$, which, when hydrolysed with dilute sulphuric acid, yields Δ^1 -*tetrahydrobenzaldehyde* (cyclohexenealdehyde), $CH_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH} \end{smallmatrix} > C \cdot COH$. This is obtained as an oil which has an odour resembling that of benzaldehyde, and forms a *semicarbazone*, $C_8H_{13}ON_3$, melting at 212—213°. Oxidation of the aldehyde by means of silver oxide leads to the formation of Δ^1 -*tetrahydrobenzoic acid*.

[With ERICH BESCHKE.]—2-Methylcyclohexane-1-ol-1-acetic acid, $CH_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} > C(OH) \cdot CH_2 \cdot CO_2H$, is formed by condensing 1-methylcyclohexane-2-one with ethyl bromoacetate in presence of zinc and hydrolysing the resulting ester; it melts at 67—68°. When heated with sodium hydrogen sulphite at 160—170°, the ethyl ester loses water, forming the *ethyl* ester of the unsaturated acid. 1-Methyl- Δ^1 -cyclohexene-2-acetic acid is obtained as an oil, which, when distilled, decomposes and yields 1-methyl-2-methylenecyclohexane,



This is obtained in a yield of 84 per cent. of the theoretical, boils at 122—125°, has a sp. gr. 0.808 and n_D 1.4516 at 22°, and is oxidised by permanganate to 1-methylcyclohexane-2-one and the *glycol*,



melting at 59—60°. Hexahydro-*o*-tolualdehyde is obtained only in small quantities when the glycol is heated with dilute acids. The *semicarbazone*, $C_9H_{17}ON_3$, crystallises from boiling water and melts at 136—137°.

The *nitrosochloride* of 1-methyl-2-methylenecyclohexane is solid; the *nitrolamine* formed with piperidine is obtained as a syrup. When heated with dilute sulphuric acid, the *oxime* obtained from the nitrosochloride yields Δ^1 -*tetrahydro-*o*-tolualdehyde*, which forms a crystalline *semicarbazone* melting at 208—212°.

The behaviour of 3-methylcyclohexeneacetic acid (Abstr., 1901, i, 156; Tétay, Abstr., 1902, i, 584) is in accordance with the constitution $CH_2 \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} > C : CH \cdot CO_2H$. The amide is now found to melt at 153—154°; when heated with phosphoric oxide, it forms the *nitrile*, $C_8H_{13} \cdot CN$, which boils at 108—112° under 10 mm., or at 230—234° under the atmospheric pressure, and has an odour resembling that of benzonitrile. With bromine in chloroform solution, the acid forms a crystalline *dibromide*, $C_9H_{14}O_2Br_2$, which melts at 127—129°, and when dissolved in an aqueous alkali carbonate gradually yields an *oil* having the properties of a monobromo-unsaturated com-

pound. 1-Methyl-3-methylenecyclohexane, $\text{CH}_2\langle\begin{smallmatrix}\text{CHMe}\cdot\text{CH}_2 \\ \text{CH}_2-\text{CH}_2\end{smallmatrix}\rangle\text{C}\cdot\text{CH}_2$, formed by slow distillation of 3-methylcyclohexeneacetic acid, boils at $123-124^\circ$, has a sp. gr. $0.794-0.797$, n_D 1.4466 at 18° or 1.4461 at 20° , and $[\alpha]_D -29^\circ$ to -30.22° , and when oxidised yields 1-methylcyclohexane-3-one and the glycol, $\text{CH}_2\langle\begin{smallmatrix}\text{CHMe}\cdot\text{CH}_2 \\ \text{CH}_2-\text{CH}_2\end{smallmatrix}\rangle\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$. This is obtained as a viscid mass, which boils at $150-153^\circ$ under 39 mm. pressure, and when heated with dilute acids yields hexahydro-*m*-tolualdehyde.

The nitrosochloride of 1-methyl-3-methylenecyclohexane, $(\text{C}_8\text{H}_{14}\text{ONCl})_2$, is obtained in a yield of 15–20 per cent. of the theoretical, and with piperidine forms the nitrolamine, $\text{C}_8\text{H}_{14}(\text{NO})\cdot\text{C}_5\text{H}_{10}\text{N}$, melting at $136-137^\circ$. The oxime of Δ^1 -tetrahydro-*m*-tolualdehyde is formed from the nitrosochloride by the action of alcoholic potassium hydroxide. The semicarbazone, $\text{C}_9\text{H}_{15}\text{ON}_3$, melts at $206-207^\circ$.

[With EDGAR EVANS.]—4-Methylcyclohexane-1-ol-1-acetic acid, $\text{CHMe}\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2\end{smallmatrix}\rangle\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, formed by condensing 1-methylcyclohexane-4-one with methyl bromoacetate and hydrolysing the resulting ester, crystallises from dilute alcohol or boiling water in two forms, of which the one obtained in the greater amount melts at $139.5-140.5^\circ$, whilst the other melts at $88-90^\circ$. 4-Methylcyclohexene-1-acetic acid melts at $42-43^\circ$ and boils at $137-138^\circ$ under 14 mm. pressure; the silver salt, $\text{C}_9\text{H}_{13}\text{O}_2\text{Ag}$, was analysed. 1-Methyl-4-methylenecyclohexane, $\text{CHMe}\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2\end{smallmatrix}\rangle\text{C}\cdot\text{CH}_2$, boils at $122-123^\circ$ and has a sp. gr. 0.7925 and n_D 1.4446 at 22° . The glycol, $\text{CHMe}\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2\end{smallmatrix}\rangle\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, crystallises readily, melts at $87-88^\circ$, and when heated with dilute acids yields principally a high boiling condensation product and a volatile oil which does not form a semicarbazone, together with only a small amount of hexahydro-*p*-tolualdehyde. The semicarbazone of this melts at $154-156^\circ$.

The nitrosochloride of 1-methyl-4-methylenecyclohexane is obtained in only a small yield; the nitrolamine formed with piperidine melts at $134-135^\circ$. Δ^1 -Tetrahydro-*p*-tolualdehyde, obtained through the oxime from the nitrosochloride, forms a semicarbazone melting at $192-194^\circ$. G. Y.

Reduction of Partially Hydrogenated Benzenes. AUGUST KLAGES and FRITZ SOMMER (*Ber.*, 1906, 39, 2306–2315).—The hydrocarbon, $\text{C}_{11}\text{H}_{16}$, obtained by Rupe and Leichtenhan (this vol., i, 374) is more readily prepared by treating the reaction-product of carvone and magnesium methyl bromide with 40 per cent. sulphuric acid at -5° ; it is regarded as 2-methyl- $\Delta^{2,6,8(9)}$ -menthatriene on account of its conversion into 2-methyl-*p*-cymene by a boiling 2 per cent. solution of hydrogen chloride in glacial acetic acid. 2-Methyl-*p*-cymene is a colourless, mobile liquid with the odour of cymene; it boils at $86-87.5^\circ$ under 16 mm. and at 198° under 732 mm. pressure, is converted into tetra-

bromo-*o*-xylene by cold bromine and aluminium, and on treatment with fuming sulphuric acid yields two sulphonic acids, the α -acid, the chloride of which is solid and forms a *sulphonanilide*, $C_{17}H_{21}O_2NS$, melting at $186-187^\circ$, and the β -acid, the chloride of which is an oil, and the *anilide*, a crystalline solid which melts at $135-136^\circ$.

2-Methyl- $\Delta^{6,8(9)}$ -menthadiene-2-ol (*2-methylcarveol*) is prepared by adding the reaction product of magnesium methyl bromide and carvone, after keeping for one hour, to an ice-cold concentrated solution of ammonium chloride; it is obtained quantitatively as a colourless oil with a faint odour, which boils at 111° under 14 mm. pressure, has a sp. gr. 0.9471 at $20.4/4^\circ$, n_D 1.4911, and $[\alpha]_D$ 36.08° at 20.4° , and is changed by anhydrous oxalic acid at 125° into *2-methyl-p-cymene*.

2-Ethyl- $\Delta^{6,8(9)}$ -menthadiene-2-ol (*2-ethylcarveol*), prepared in similar manner, is a colourless oil which boils at $118.5-119.5^\circ$ under 14 mm. pressure, has a sp. gr. 0.9302 at $21^\circ/4^\circ$, n_D 1.4879, and $[\alpha]_D$ 31.17° at 21° .

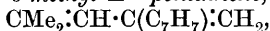
2-Ethyl- $\Delta^{2,6,8(9)}$ -menthatriene, obtained in similar manner to the methyl compound, is a colourless, mobile oil which boils at $100-101^\circ$ under 13.5 mm. pressure, has a sp. gr. 0.8859 at $18^\circ/4^\circ$, n_D 1.5041, and $[\alpha]_D$ 86.19° at 18° , and is converted by 2 per cent. hydrogen chloride in glacial acetic acid into *2-ethylcymene*, $C_{12}H_{18}$, a colourless oil which boils at 103° under 19 mm. and at 214° under 754 mm. pressure, has a sp. gr. 0.8665 at $21.1^\circ/4^\circ$, n_D 1.4965 at 21.1° , is easily soluble in sulphuric acid, and is converted by bromine and aluminium into *pentabromotoluene*, which forms long, colourless needles and melts at 283° .

2-Phenyl- $\Delta^{6,8(9)}$ -menthadiene-2-ol (*2-phenylcarveol*) is a colourless oil which boils at $159-160^\circ$ under 12 mm. pressure, has a sp. gr. 1.0156 at $15.1^\circ/4^\circ$, n_D 1.5562, and $[\alpha]_D$ 81.42° at 15.1° .

2-Phenyl- $\Delta^{2,6,8(9)}$ -menthatriene, containing a little *2-phenyl-p-cymene*, boils at $152-153^\circ$ under 13 mm. pressure, has a sp. gr. 0.9882 at $13.8^\circ/4^\circ$, n_D 1.5631, and $[\alpha]_D$ 110.2° at 13.8° , and is converted by hydrogen chloride in glacial acetic acid into *2-phenyl-p-cymene*, which can also be obtained from *2-phenylcarveol* by anhydrous oxalic acid at 120° or by hydrogen chloride and pyridine at 140° ; it is a highly refractive, colourless oil which boils at 268° under 752 mm., or at $153-154^\circ$ under 14 mm. pressure, has a sp. gr. 0.9822 at $13.8^\circ/4^\circ$, n_D 1.5670 at 13.8° , and readily forms a sulphonic acid with fuming sulphuric acid.

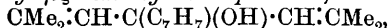
C. S.

Action of Magnesium Benzyl Chloride on Mesityl Oxide and Phorone. THEODOR VON FELLEBERG (*Ber.*, 1906, 39, 2064-2066. Compare *Abstr.*, 1904, i, 961).— β -Hydroxy- β -benzyl- δ -methyl- Δ^{γ} -pentene, $CM_e_2 \cdot CH \cdot C(C_7H_7)Me \cdot OH$, prepared from mesityl oxide, is a faintly yellow, somewhat viscous liquid with an agreeable odour; it is slightly volatile in steam, and by distillation under the ordinary pressure yields β -benzyl- δ -methyl- $\Delta^{\alpha\gamma}$ -pentadiene,



which is a colourless, mobile liquid with an odour of dimethylpentadiene; it boils at $234-236^\circ$ under 730 mm. pressure.

δ -Hydroxy- δ -benzyl- $\beta\zeta$ -dimethyl- $\Delta^{\beta\epsilon}$ -heptadiene,



obtained from phorone, is a viscous, faintly yellow liquid with a pleasant aromatic odour; it is slightly volatile in steam, and by distillation, even under 12 mm. pressure, loses water, forming δ -benzylidene- $\beta\zeta$ -dimethyl- Δ^8 -heptadiene, $\text{CMe}_2\cdot\text{CH}\cdot\text{C}(\cdot\text{CHPh})\cdot\text{CH}\cdot\text{CMe}_2$, which, after repeated distillation, is obtained as a nearly colourless, mobile liquid boiling at 277—278° under 724 mm. pressure. C. S.

Oxidation of Diphenyl Diselenide. M. STOECKER and FRIEDRICH KRAFFT (*Ber.*, 1906, **39**, 2197—2201. Compare Krafft and Lyons, *Abstr.*, 1896, i, 304).—The nitrate of phenylselenious acid melts and detonates at about 112°; when dissolved in water, neutralised with ammonia, and treated with silver nitrate, it yields *silver phenylselenite*, SePhO_2Ag , which is obtained as a crystalline precipitate. The *barium*, $(\text{SePhO}_2)_2\text{Ba}$, and *copper*, $(\text{SePhO}_2)_2\text{Cu}$, salts are described. The free *acid*, $\text{SePhO}_2\text{H}\cdot\text{H}_2\text{O}$ or $\text{SePh}(\text{OH})_3$, prepared by the action of *N*/10 hydrochloric acid on the silver salt, forms a white, crystalline mass, melts at 122—124°, loses H_2O at 100—130° under 15 mm. pressure, and then melts and decomposes at 170°. On reduction with zinc and hydrochloric acid, it forms *phenyl hydrogen selenide*, SeHPh , which boils at 183° and is oxidised by air, forming diphenyl diselenide.

The oxidation of diphenyl diselenide by chlorine in aqueous solution at 50° leads to the formation of *phenylselenic acid*, SePhO_3H , which is isolated in the form of its white, crystalline *silver* salt, SePhO_3Ag ; this detonates feebly when heated. The *barium*, $(\text{SePhO}_3)_2\text{Ba}$; *copper*, $(\text{SePhO}_3)_2\text{Cu}$; and *cadmium*, $(\text{SePhO}_3)_2\text{Cd}$, salts are described. The free *acid* is obtained as a hygroscopic syrup, which is stable when dried at 105°, detonates at 180—190°, forming phenyl diselenide, phenyl selenide, and free selenium, and in moist air forms a *hydrate*, crystallising in glistening prisms. The acid is reduced by concentrated hydrochloric acid, forming phenylselenious acid.

Both these acids deposit red selenium more or less quickly when exposed to light. G. Y.

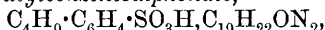
Alkaloidal Salts of *i*-sec-butylbenzenesulphonic Acid. AUGUST KLAGES (*Ber.*, 1906, **39**, 2131—2135).—Since Klages and Sautter have shown (*Abstr.*, 1904, i, 302) that optically active benzene hydrocarbons can be formed from their sulphonic acids without undergoing racemisation, the author has attempted to resolve *r*-sec-butylbenzenesulphonic acid into its optically active components by the aid of alkaloids. The results were negative.

sec-Butylbenzene, CHMeEtPh , is sulphonated and converted into the barium sulphate, which, by the action of phosphorus pentachloride, yields *sec-butylbenzenesulphonic chloride* as a colourless oil, which boils at 179—180° under 20 mm. pressure and has a sp. gr. 1.202 at 16.4°/4°; the *anilide* melts at 63—64° and the *sulphonamide* at 80—81°.

Quinine sec-butylbenzenesulphonate, $\text{C}_4\text{H}_9\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}\cdot\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2$, prepared by the addition of quinine sulphate to barium *sec*-butylbenzenesulphonate, is sparingly soluble in water, from which it separates in needles. When dried at 110°, it melts at 184° and

has $[\alpha]_D -10.5^\circ$ at 20° in methyl-alcoholic solution ($c=1.238$). It was not found possible to separate it into two isomeric quinine salts.

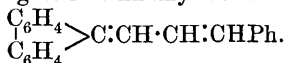
Cinchonidine sec-butylbenzenesulphonate,



forms glistening needles and, when dried at 110° , melts at 205° . It has $[\alpha]_D -7.34^\circ$ at 20° in methyl-alcoholic solution ($c=1$). The brucine salt is oily.

Strychnine sec-butylbenzenesulphonate, $C_4H_9 \cdot C_6H_4 \cdot SO_3H, C_{21}H_{22}O_2N_2$, separates from benzene in needles, melts at $189-190^\circ$, and in methyl-alcoholic solution ($c=0.846$) is optically inactive. A. McK.

Derivatives of Fulvene. I. Condensation of Indene with Aldehydes. JOHANNES THIELE and ADOLF BÜHNER (*Annalen*, 1906, 347, 249—274. Compare Thiele, Abstr., 1900, i, 298; 1901, i, 76; Kipping and Hall, Trans., 1900, 77, 471; Marckwald, Abstr., 1900, i, 434).—The ethylene linking lying outside of the ring of fulvene derivatives is readily reduced by aluminium amalgam in moist ethereal solution if a hydrogen atom of the methylene group is substituted by phenyl or carboxyl. The phenyl group may be attached by an intermediate ethylene linking as in cinnamylidene fluorene,



Whilst bisdiphenylene-ethylene is reduced to bisdiphenylene-ethane (compare De la Harpe and van Dorp, Abstr., 1876, i, 242), tetraphenylethylene is not reduced by aluminium amalgam.

1-Benzylindene, $CH_2 < \begin{array}{c} C_6H_4 \\ | \\ CH \end{array} > C \cdot CH_2Ph$, formed by reducing benzylideneindene, is obtained as an almost colourless oil, which boils at $183-185^\circ$ under 13 mm. pressure, is oxidised slowly by air, becoming yellow, gives a yellow coloration with concentrated sulphuric acid, and forms with bromine a *dibromide*, and with amyl nitrite and hydrochloric acid a solid, unstable *nitrosochloride*. It condenses with benzaldehyde in presence of methyl-alcoholic potassium hydroxide, forming 1-benzyl-3-benzylideneindene, $CHPh:C < \begin{array}{c} C_6H_4 \\ | \\ CH \end{array} > C \cdot CH_2Ph$ (compare Abstr., 1901, i, 76). This crystallises from alcohol in glistening, yellow leaflets, melts at $137-137.5^\circ$, and gives a violet coloration with concentrated sulphuric acid. It is formed also by distillation at $250-260^\circ$ under 12 mm. pressure of the colourless hydrocarbon obtained previously (Abstr., 1901, i, 76) by reduction of chlorobenzylbenzylideneindene, $CHPh:C < \begin{array}{c} C_6H_4 \\ | \\ CH \end{array} > C \cdot CHClPh$. The results of ebullioscopic molecular weight determinations with the colourless hydrocarbon agree with the formula $C_{23}H_{18}$.

1:3-Dibenzylindene, $CH_2Ph \cdot C < \begin{array}{c} C_6H_4 \\ | \\ CH \end{array} > CH \cdot CH_2Ph$, is formed by reduction of benzylbenzylideneindene; it crystallises from light petroleum in stout, colourless prisms, or from methyl alcohol in white leaflets, melts at $62-63^\circ$, when treated with amyl nitrite and hydrochloric acid forms an unstable *nitrosochloride*, and reacts with bromine

in chloroform solution, forming a *dibromide*, $C_{23}H_{20}Br_2$, which separates from light petroleum in stout, colourless crystals and melts and decomposes at $103-104^\circ$. When boiled with pyridine, the dibromide loses $2HBr$, forming benzylbenzylideneindene.

On preparing Marckwald's viscid benzylidene (*loc. cit.*) and distilling the product in a vacuum, the authors obtained a large fraction which is identical with the product of the reduction of benzylideneindene.

Marckwald's 1-methylindene has been compared and found to be identical with Roser's 3-methylindene (Abstr., 1888, 1303).

3-Benzylidene-1-methylindene, $CMe \leq \begin{smallmatrix} C_6H_4 \\ CH \end{smallmatrix} > C:CHPh$ (compare Marckwald, *loc. cit.*), is prepared by the condensation of methylindene with benzaldehyde; it crystallises from methyl alcohol, melts at $43-44^\circ$, and gives a reddish-violet coloration with concentrated sulphuric acid. On reduction, it yields 3-benzyl-1-methylindene (?) as a colourless oil, which combines with 1 mol. of bromine, but does not form condensation products.

3-Anisylidene-1-methylindene, $CMe \leq \begin{smallmatrix} C_6H_4 \\ CH \end{smallmatrix} > C:CH \cdot C_6H_4 \cdot OMe$, formed by the condensation of methylindene with anisaldehyde, crystallises from alcohol in glistening, yellow leaflets, melts at 113° , and gives a violet-blue coloration with concentrated sulphuric acid.

The action of anisaldehyde on indene in presence of methyl-alcoholic potassium hydroxide leads to the formation of anisylideneindene and hydroxyanisylanisylideneindene, which are separated by fractional crystallisation from alcohol.

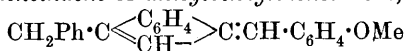
1-Anisylideneindene, $CH \leq \begin{smallmatrix} C_6H_4 \\ CH \end{smallmatrix} > C:CH \cdot C_6H_4 \cdot OMe$, is obtained as a reddish-yellow, crystalline powder, melts at $118-119^\circ$, and gives a greenish-brown coloration with concentrated sulphuric acid. When reduced with aluminium amalgam, it yields 1-anisylindene, $CH_2 \leq \begin{smallmatrix} C_6H_4 \\ CH \end{smallmatrix} > C \cdot CH_2 \cdot C_6H_4 \cdot OMe$, which crystallises in white leaflets, melts at $63-64^\circ$, and condenses with anisaldehyde, forming 3-anisyl-1-anisylideneindene,

$OMe \cdot C_6H_4 \cdot CH_2 \cdot C \leq \begin{smallmatrix} C_6H_4 \\ CH \end{smallmatrix} > C:CH \cdot C_6H_4 \cdot OMe$,
crystallising in yellow leaflets and melting at $111-112^\circ$.

α -Hydroxyanisylanisylideneindene,

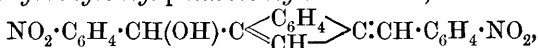
$OMe \cdot C_6H_4 \cdot CH(OH) \cdot C \leq \begin{smallmatrix} C_6H_4 \\ CH \end{smallmatrix} > C:CH \cdot C_6H_4 \cdot OMe$,
crystallises from benzene in small, lemon-yellow leaflets, melts at $141.5-142.5^\circ$, gives a bluish-green coloration with concentrated sulphuric acid, and on reduction yields *α -hydroxydianisylindene*, $OMe \cdot C_6H_4 \cdot CH(OH) \cdot CH \leq \begin{smallmatrix} C_6H_4 \\ CH \end{smallmatrix} > C \cdot CH_2 \cdot C_6H_4 \cdot OMe$. This separates from a mixture of alcohol and ether as a colourless, flocculent substance melting at $175-178^\circ$, or from alcohol in a vacuum as a colourless, viscid oil, and when treated with alcoholic potassium hydroxide is converted into anisylanisylideneindene.

Benzylanisylideneindene or *anisylbenzylideneindene*,



or $\text{CHPh} \cdot \text{C} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CH} \end{array} \text{C} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, is formed by the action of anisaldehyde on benzylindene or of benzaldehyde on anisylindene; it crystallises from alcohol, melts at 132—133°, and gives an indigo-blue coloration with concentrated sulphuric acid. The identity of the products of the two methods of formation is explained by assuming an oscillation of the ethylene linking (compare Knorr, Abstr., 1894, i, 543; Fischer and Rigaud, Abstr., 1902, i, 188).

p-Nitro-α-hydroxybenzyl-p-nitrobenzylideneindene,



prepared by the condensation of indene with *p*-nitrobenzaldehyde in presence of a small quantity of an alkali hydroxide, forms yellow crystals and melts and decomposes at 216—217°.

The reduction of hydroxybenzylbenzylideneindene with aluminium amalgam in moist ethereal solution leads to the formation of the colourless isomeride of benzylbenzylideneindene, together with *hydroxydibenzylindene*, $\text{OH} \cdot \text{CHPh} \cdot \text{CH} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CH} \end{array} \text{C} \cdot \text{CH}_2\text{Ph}$, which is obtained as a viscid oil. When distilled in a vacuum, it decomposes, yielding benzaldehyde, benzylbenzylideneindene, and a brown resin, and when treated with alcoholic potassium hydroxide loses water, forming benzylbenzylideneindene.

The residues from the commercial indene used in the above condensations, after complete removal of the indene, yielded an oil which boiled at the same temperature as indene, and on analysis gave figures pointing to the presence of coumarone together with a small amount of hydrindene (compare Weger and Billmann, Abstr., 1903, i, 332).

G. Y.

Derivatives of Fulvene. III. Condensation Products of Fluorene. JOHANNES THIELE and FRANZ HENLE (*Annalen*, 1906, 347, 290—315. Compare preceding abstract).—The reactivity of the methylene group of fluorene is less than that of indene, which is itself less reactive than *cyclopentadiene*, that is, the activity decreases as the ethylene linkings of the five-atom ring are rendered inactive by benzene nuclei. The colour of these three substances diminishes in the same order.

Fluorene does not react with aliphatic aldehydes, or with ketones, or with amyl nitrite and sodium ethoxide, but forms condensation products with aromatic aldehydes in presence of alcoholic alkali hydroxides. These products form additive compounds with bromine, and are reduced by aluminium amalgam and moist ether, yielding hydrocarbons of which those having an ethylene linking in the α-position to a phenyl group form additive compounds with picric acid.

Benzylidenefluorene (Abstr., 1900, i, 347) crystallises in rhombic

prisms [$a:b:c=0.9942:1:2.6859$], is less soluble than fluorene in organic solvents, and decolorises potassium permanganate in sodium carbonate solution. The *picrate*, $C_{20}H_{14}, C_6H_3O_7N_3$, crystallises in orange needles, melts at $115-116^\circ$, and is decomposed by water. The *dibromide*, $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > CBr \cdot CHBrPh$, forms glistening prisms, melts at 112° , and on treatment with zinc dust and glacial acetic acid yields benzylidenefluorene.

Benzylfluorene, $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > CH \cdot CH_2Ph$, formed by reduction of the benzylidene compound with sodium and amyl alcohol, or in better yield by means of aluminium amalgam, crystallises from light petroleum, melts at $130-131^\circ$, and gives with concentrated sulphuric acid a violet coloration, becoming blue and finally disappearing on addition of water.

The action of benzyl chloride and potassium hydroxide on fluorene in a sealed tube at 270° , or on benzylfluorene at 230° , leads to the formation of dibenzylfluorene, which is identical with Weissgerber's supposed benzylfluorene (Abstr., 1901, i, 521). It crystallises in thin prisms and melts at $147-148^\circ$.

Anisylidenefluorene, $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > C:CH \cdot C_6H_4 \cdot OMe$, crystallises from glacial acetic acid or ethyl acetate in stout, yellow prisms, melts at $128-129^\circ$, is resinified by sulphuric acid and zinc chloride, and on reduction yields *anisylfluorene*, $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > CH \cdot CH_2 \cdot C_6H_4 \cdot OMe$. This crystallises from light petroleum in plates and melts at $108-108.5^\circ$.

Furfurylidenefluorene, $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > C:CH \cdot C_4H_3O$, crystallises from alcohol in yellow needles. *Furfurylfluorene*, $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > CH \cdot CH_2 \cdot C_4H_3O$, crystallises in stout, colourless, rhombic prisms and melts at $91-92^\circ$.

Bisdiphenylene-ethane, formed by reduction of bisdiphenylene-ethylene with aluminium amalgam, melts at $239-240^\circ$ (De la Harpe and van Dorp, Abstr., 1876, i, 242).

Cinnamylidenefluorene, $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > C:CH:CH:CHPh$, is prepared by the action of cinnamaldehyde and sodium ethoxide on fluorene in absolute alcoholic solution at 55° ; it crystallises from glacial acetic acid in lemon-yellow needles and melts at 154.5° . The *picrate*, $C_{22}H_{16}, 2C_6H_3O_7N_3$, crystallises in needles and melts at $178-179^\circ$.

The *picrate* of $\alpha\delta$ -diphenyl- $\Delta^{\alpha\gamma}$ -butadiene, $C_{16}H_{14}, 2C_6H_3O_7N_3$ (Thiele and Schleussner, Abstr., 1899, i, 612), crystallises in yellowish-red needles and melts at $152-153^\circ$.

Cinnamylidenefluorene dibromide, $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > C:CH \cdot CHBr \cdot CHBrPh$, formed by the action of bromine on the hydrocarbon in chloroform solution, crystallises in yellow prisms or needles, melts and decomposes

at 127°, is decomposed by solvents of high boiling point, and regenerates cinnamylidenefluorene when treated with zinc dust and glacial acetic acid at the ordinary temperature. When oxidised by means of chromic acid in glacial acetic acid solution at 25—30°, it yields dibromodihydrocinnamic acid and fluorenone. The *tetrabromide*, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CBr} \cdot [\text{CHBr}]_2 \cdot \text{CHBrPh}$, is formed by the action of bromine on cinnamylidenefluorene in chloroform solution exposed to bright sunshine; it forms sheaves of crystals, melts and decomposes at about 160°, and yields cinnamylidenefluorene when treated with zinc dust and glacial acetic acid.

The reduction of cinnamylidenefluorene leads to the formation of bismonohydrocinnamylidenefluorene, which separates from the light petroleum extract of the reduction product, Δ^β -dihydrocinnamylidenefluorene, which remains dissolved in the light petroleum, and a hydrocarbon, $(\text{C}_{22}\text{H}_{17})_x$, which is insoluble in light petroleum.

Δ^β -Dihydrocinnamylidenefluorene, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CH} \cdot \text{CH} : \text{CH} \cdot \text{CH}_2\text{Ph}$,

separates from alcohol in long, almost colourless, slightly shimmering crystals, melts at 88°, is readily soluble in acetone, ether, benzene, toluene, chloroform, or glacial acetic acid, does not form a picrate, reduces ammoniacal silver nitrate solution at the ordinary temperature, and gives with benzaldehyde and much concentrated sulphuric acid an intense red coloration which is destroyed by addition of water. The *dibromide*, $\text{C}_{22}\text{H}_{18}\text{Br}_2$, crystallises in matted needles, melts at 133°, and forms the Δ^β -dihydro-compound when treated with zinc dust and glacial acetic acid, or when heated with methyl-alcoholic potassium hydroxide.

When boiled with sodium ethoxide or piperidine in alcoholic solution, Δ^β -dihydrocinnamylidenefluorene is converted into the

Δ^α -dihydro-isomeride, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{C} : \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Ph}$ or $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CH} \cdot \text{CH}_2 \cdot \text{CH} : \text{CHPh}$,

which crystallises from alcohol in small, white leaflets, melts at 81—82°, and forms a *picrate*, $\text{C}_{22}\text{H}_{18} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$. This crystallises in glistening, reddish-yellow needles and melts at 128—129°. The *dibromide*, $\text{C}_{22}\text{H}_{18}\text{Br}_2$, crystallises from light petroleum, melts at 94—96°, is decomposed by potassium hydroxide, and forms Δ^α -dihydrocinnamylidenefluorene when treated with zinc dust and glacial acetic acid.

Bismonohydrocinnamylidenefluorene, $(\text{C}_{22}\text{H}_{17})_2$, separates from light petroleum in crystals containing petroleum and melting at about 120°, from acetone in crystals containing acetone and melting at 112—115°, or from glacial acetic acid in glistening crystals, $\text{C}_{44}\text{H}_{34} \cdot \text{C}_2\text{H}_4\text{O}_2$, melting at 124°. The hydrocarbon melts at 160—161° and is readily soluble in hot acetone, benzene, toluene, or chloroform.

The *hydrocarbon*, $(\text{C}_{22}\text{H}_{17})_x$, crystallises from nitrobenzene, melts at 257° (corr.), and evolves hydrogen bromide when heated with bromine. G. Y.

New Method for the Preparation of Tetraphenylmethane. MARTIN FREUND (*Ber.*, 1906, **39**, 2237—2238).—Tetraphenylmethane is one of the products resulting from the action of magnesium phenyl bromide on triphenylmethyl bromide; triphenylmethyl peroxide is also formed. A. McK.

Organic Double Salts with Bismuth Chloride. LUDWIG VANINO and F. HARTL (*Arch. Pharm.*, 1906, **244**, 216—220).—Compounds of bismuth chloride with the following bases were obtained by mixing the constituents in acetone, alcohol, or other solution. They are crystalline; and some are, others are not, decomposed by water.

Diphenylamine, $\text{NHPh}_2, \text{BiCl}_3$. *Nitrosodiphenylamine*,

$\text{NO} \cdot \text{NPh}_2, \text{BiCl}_3$.

Nitrosodimethylaniline, $2\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2, 3\text{BiCl}_3$. *Aldehyde-ammonia* (really a compound with a polymeric ethylideneimine).

$(\text{CHMe} \cdot \text{NH})_3, 3\text{BiCl}_3$.

Methylamine hydrochloride, $3\text{NH}_3\text{MeCl}, 2\text{BiCl}_3$. *Rheumatine*,

$\text{C}_{34}\text{H}_{34}\text{O}_7\text{N}_2, 2\text{BiCl}_3$.

Quinaphenine, $2\text{C}_{27}\text{H}_{29}\text{O}_3\text{N}_3, 5\text{BiCl}_3$. *Piperazine*, $2\text{C}_4\text{H}_{10}\text{N}_2, 3\text{BiCl}_3$.

C. F. B.

Formation of Bases from Acetophenone, Formaldehyde, and Ammonium Chloride. H. SCHÄFER and BERNHARD TOLLENS (*Ber.*, 1906, **39**, 2181—2189. Compare Marle and Tollens, *Abstr.*, 1903, i, 493; Tollens, *Abstr.*, 1904, i, 507).—The action of formaldehyde and ammonium chloride on acetophenone leads to the formation of *s*-triphenacylomethylamine, *s*-diphenacylomethylamine, and possibly phenacylomethylamine hydrochlorides.

s-Triphenacylomethylamine hydrochloride, $\text{N}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{COPh})_3, \text{HCl}$, is extracted from the cold reaction product by means of chloroform; it crystallises in white, microscopic needles, melts at 200 — 201° , and in dilute alcoholic solution forms precipitates with the alkaloid reagents. The free base, $\text{N}(\text{C}_9\text{H}_9\text{O})_3, \frac{1}{2}\text{H}_2\text{O}$, crystallises from ether in monoclinic needles. The *sulphate*, $2\text{N}(\text{C}_9\text{H}_9\text{O})_3, \text{H}_2\text{SO}_4$, melts at 180 — 181° ; the *nitrate*, $\text{N}(\text{C}_9\text{H}_9\text{O})_3, \text{HNO}_3, \frac{1}{2}\text{H}_2\text{O}$, forms microscopic needles and melts at 142 — 143° ; the *platinichloride*, $(\text{C}_{27}\text{H}_{27}\text{O}_3\text{N})_2, \text{H}_2\text{PtCl}_6$, forms a dark yellow, crystalline precipitate and melts at 207° . When boiled with aqueous hydroxylamine in a reflux apparatus, the base evolves ammonia and yields an oil smelling of cinnamaldehyde. In one case, a substance melting at 228° was obtained by boiling the hydrochloride of the base with hydroxylamine hydrochloride in alcoholic solution. With phenylhydrazine, the base forms the phenylhydrazone of phenylvinyl ketone (Moureu, *Abstr.*, 1894, i, 30), which crystallises in yellow, monoclinic needles, melts at 152 — 153° , and dissolves in ether, light petroleum, or benzene, forming solutions with deep blue fluorescence. Phenyl vinyl ketone is formed when *s*-triphenacylomethylamine hydrochloride is distilled in a current of steam.

The action of phenylhydrazine on the dibromide of phenyl vinyl ketone leads to the formation of phenylhydrazine hydrobromide.

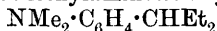
s-Diphenacylomethylamine hydrochloride, $\text{NH}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{COPh})_2, \text{HCl}$, remains in the distillation residue when *s*-triphenacylomethylamine-

hydrochloride is heated in a current of steam. It forms a white, crystalline mass, melts when not pure at 136—138°, and forms a *platinichloride*, $(C_{18}H_{19}O_2N)_2 \cdot H_2PtCl_6$, melting at about 155°.

G. Y.

Dialkylaminobenzaldehydes. IV. FRANZ SACHS and FRANZ MICHAELIS (*Ber.*, 1906, **39**, 2163—2171. Compare Sachs and Steinert, *Abstr.*, 1904, i, 506; F. and L. Sachs, *Abstr.*, 1905, i, 202).—*Trinitro-p-dimethylaminoisopropylbenzene*, $C_{11}H_{14}N(NO_2)_3$, prepared by nitrating dimethylamino-*p*-isopropylbenzene, $NMe_2 \cdot C_6H_4 \cdot CHMe_2$, formed by the action of magnesium methyl iodide on *p*-dimethylaminobenzaldehyde (Sachs and Sachs, *loc. cit.*), separates from dilute alcohol in bluish-yellow needles and melts at 112°.

Trinitro-p-dimethylaminoisoamylbenzene, $NMe_2 \cdot C_6H(NO_2)_3 \cdot CHEt_2$, prepared by nitrating *p*-dimethylaminoisoamylbenzene,



(Sachs and Sachs, *loc. cit.*), separates from alcohol in yellow, hexagonal crystals and melts at 65°.

p-Dimethylaminoisooheptylbenzene, $NMe_2 \cdot C_6H_4 \cdot CHPr_2$, prepared by the action of magnesium propyl bromide on *p*-dimethylaminobenzaldehyde, is a yellow oil and boils at 164° under 24 mm. pressure.

p-Dimethylaminophenyldiisobutylmethane, $NMe_2 \cdot C_6H_4 \cdot CH(C_4H_9)_2$, prepared from magnesium butyl iodide and *p*-dimethylaminobenzaldehyde, is a yellow oil which boils at 236° under 13 mm. pressure. It gives a reddish-brown coloration with potassium dichromate and sulphuric acids.

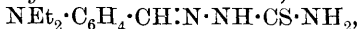
p-Dimethylaminophenyldibenzylmethane, $NMe_2 \cdot C_6H_4 \cdot CH(CH_2Ph)_2$, prepared from magnesium benzyl chloride and *p*-dimethylaminobenzaldehyde, separates from dilute alcohol in tetragonal prisms and melts at 82°. It gives a dark red coloration with potassium dichromate and sulphuric acid.

p-Dimethylaminophenyldinaphthylmethane, $NMe_2 \cdot C_6H_4 \cdot CH(C_{10}H_7)_2$, prepared from magnesium α -naphthyl bromide and *p*-dimethylaminobenzaldehyde, crystallises from carbon disulphide in snow-white needles and melts at 223°.

p-Diethylaminoisopropylbenzene, $NEt_2 \cdot C_6H_4 \cdot CHMe_2$, prepared from magnesium methyl iodide and *p*-diethylaminobenzaldehyde, is a yellow oil and boils at 156° under 43 mm. pressure.

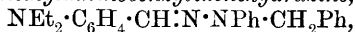
p-Diethylaminoisooheptylbenzene, $NEt_2 \cdot C_6H_4 \cdot CHPr_2$, prepared from magnesium propyl bromide and *p*-diethylaminobenzaldehyde, is a yellow oil and boils at 165° under 22 mm. pressure.

p-Diethylaminobenzylidenethiosemicarbazide,



prepared from *p*-diethylaminobenzaldehyde and thiosemicarbazide, forms tetragonal prisms and melts at 180°.

Phenylbenzyl-p-diethylaminobenzylidenehydrazine,



prepared from *p*-diethylaminobenzaldehyde and phenylbenzylhydrazine, separates from alcohol in tetragonal prisms and melts at 123°.

p-Diethylaminobenzylideneacetone, $NEt_2 \cdot C_6H_4 \cdot CH:CH \cdot COMe$, prepared by the addition of acetone and a few drops of alkali to a solu-

tion of *p*-ethylaminobenzaldehyde in alcohol, separates in reddish-yellow, spear-shaped crystals and melts at 164°.

p-Diethylaminobenzylidenemalononitrile, $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C}(\text{CN})_2$, prepared from *p*-diethylaminobenzaldehyde and malononitrile in presence of a little piperidine, separates from alcohol in yellowish-red, rhombic prisms and melts at 130°.

p-Diethylaminobenzylidenebenzyl cyanide, $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CPh} \cdot \text{CN}$, prepared from *p*-diethylaminobenzaldehyde and benzyl cyanide, crystallises from alcohol in yellow, prismatic needles, and melts at 97°.

p-Diethylaminobenzylidene-*p*-nitrobenzyl cyanide,
 $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C}(\text{CN}) \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$,
 prepared from *p*-diethylaminobenzaldehyde and *p*-nitrobenzyl cyanide, separates from glacial acetic acid in dark red needles and melts at 206°.

p-Diethylaminobenzylidenerhodanic acid,

$$\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C} \begin{array}{l} \text{CO} \cdot \text{CS} \\ \text{S} - \text{NH} \end{array}$$
,
 prepared from *p*-diethylaminobenzaldehyde and rhodanic acid, separates from alcohol in dark red needles and melts at 182°.

p-Diethylaminobenzylidenearbituric acid,

$$\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C} \begin{array}{l} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{array} > \text{CO}$$
,
 prepared from *p*-diethylaminobenzaldehyde and barbituric acid, separates from glacial acetic acid in red needles and melts at 129°.

p-Diethylaminobenzylidenecyanoacetamide,
 $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C}(\text{CN}) \cdot \text{CO} \cdot \text{NH}_2$,
 prepared from *p*-diethylaminobenzaldehyde and cyanoacetamide in the presence of a little piperidine, separates from alcohol in orange, rhombic prisms and melts at 134.5°.

A. McK.

Pseudo-acids. ARTHUR HANTZSCH (*Ber.*, 1906, 39, 2098—2112); HANS EULER (*ibid.*, 2265—2269).—Polemical (compare this vol., i, 415). C. S.

Imide Bromides and their Decomposition. JULIUS VON BRAUN and CARL MÜLLER (*Ber.*, 1906, 39, 2018—2022. Compare *Abstr.*, 1904, i, 688, 731, 841, 918; 1905, i, 634, 636).—The imide bromides, prepared by the action of phosphorus pentabromide on fatty or aromatic amides, resemble the imide chlorides, but are more readily hydrolysed by moisture. Amides of aliphatic acids react energetically with phosphorus pentabromide, the final products being basic substances which do not form the amide when treated with water.

Benzanilide and phosphorus pentabromide interact, forming the imide bromide, which is obtained as a reddish-yellow, crystalline cake, decomposes when distilled, and with water forms benzanilide. Methylbenzamide, when mixed with phosphorus pentabromide at the ordinary temperature, forms the imide bromide, which, when slightly

heated, decomposes into methyl bromide and benzonitrile, a small residue containing cyaphenine remaining on distillation of the products. Similarly, benzylbenzamide yields benzyl bromide and benzonitrile. The imide bromides may be isolated if the reaction with phosphorus pentabromide is carried out in chloroform solution.

The action of phosphorus pentabromide on dibenzoylhexamethylenediamine and on dibenzoylheptamethylenediamine leads to the formation of $\alpha\zeta$ -dibromohexane and $\alpha\eta$ -dibromoheptane, which, on treatment with sodium phenoxide, yield $\alpha\zeta$ -diphenoxyhexane and $\alpha\eta$ -diphenoxyheptane respectively. G. Y.

Action of Nitrous Acid on Tolyl- and *m*-Xylyl-carbamides and on Phenylthiocarbamide. II. J. HAAGER and R. DOHR (*Monatsh.*, 1906, 27, 267—279. Compare Abstr., 1904, i, 236; Walther and Wlodkowsky, Abstr., 1899, i, 590).—Nitrous acid reacts with *m*- and *p*-tolylcarbamides in the same manner as with phenylcarbamide, forming the nitroso-derivatives in presence of a limited quantity, but the carbamides in presence of an excess, of hydrochloric acid. *o*-Tolyl- and *m*-xylyl-carbamides yield the corresponding carbimides, but not the nitroso-derivatives. Nitrous acid does not react with α - and β -naphthylcarbamides in hydrochloric acid solution.

m-Tolylcarbimide, C_8H_7ON , boils at 183° and behaves towards water, absolute alcohol, and pyridine in the same manner as other carbimides.

Nitroso-*p*-tolylcarbamide melts and decomposes at 85° (83° ; Walther and Wlodkowsky, *loc. cit.*).

m-Xylyl-4-carbimide, $C_8H_5Me_2 \cdot NCO$, formed from *m*-xylyl-4-carbamide by the action of nitrous acid in hydrochloric or of sodium nitrite in glacial acetic acid solution, is obtained as a yellow oil, which boils at 215° and is more stable than other carbimides towards water.

The acid filtrates from the preparation of the nitrosocarbamides and of the carbimides contain the corresponding diazonium chlorides.

Whilst the chief product of the interaction of nitrous acid and phenylthiocarbamide is dianilino-*o*-diazothiolo, which melts at 190° (181° ; Hector, Abstr., 1889, 872; 1890, 526), a portion of the thiocarbamide reacts with the nitrous acid in the same way as does phenylcarbamide, forming phenylcarbimide. G. Y.

Constitution and Colour of Nitrophenols. HUGO KAUFFMANN (*Ber.*, 1906, 39, 1959—1966. Compare Abstr., 1900, i, 480; 1901, i, 318).—The author criticises Hantzsch's views (this vol., i, 353) and concludes that whilst the "quinone theory" of colour explains the colour of nitrophenols, which, according to the "auxochrome theory," should be less highly coloured than the corresponding ethers, the latter theory is of more general applicability.

Contrary to Hantzsch's statement that all nitrophenol ethers incapable of exhibiting tautomerism are colourless, nitroquinol dimethyl ether is yellow. In agreement with the "auxochrome theory" is the colour of sodium *m*-nitrophenoxides and the formation of yellow nitro-derivatives by hydrocarbons, such as chrysene and pyrene.

The methoxy-, acetoxy-, and acetyl-amino-groups and iodine are only weak, whilst the nitro-, amino-, and dialkyl-amino-groups are strong auxochromes. The auxochromic influence of bromine is weak and uncertain; that of chlorine is negative. G. Y.

Nitrophenolsulphonic Acids. ROBERT GNEHM and OSKAR KNECHT (*J. pr. Chem.*, 1906, [ii], 73, 519—537).—Whilst *o*-nitrophenol-*p*-sulphonic acid is formed by the action of fuming sulphuric acid (Kekulé, *Jahresber.*, 1867, 641) or of chlorosulphonic acid on *o*-nitrophenol (Mazurowska, this Journal, 1875, 875; 1876, ii, 61), sulphonation of *o*-nitrophenol in presence of mercury (Iljinski, *Abstr.*, 1904, i, 176; Schmidt, *ibid.*, 256) leads to the formation of a mixture of sulphonic acids, of which *o*-nitrophenoltrisulphonic acid is isolated in the form of its barium salt, $C_6H_3O_{12}NS_3Ba_2$.

o-Nitrophenol-*p*-sulphonic acid crystallises from chloroform in glistening prisms, loses $CHCl_3$ at 80—90°, and melts at 141—142°. The potassium salt crystallises with 1 mol. of water.

m-Nitrophenolsulphonic acid, $NO_2 \cdot C_6H_3(OH) \cdot SO_3H$, formed from *m*-nitrophenol by the action of fuming sulphuric acid, or in small yields by sulphonation in presence of mercury, crystallises in large, colourless, transparent, hexagonal leaflets containing $4H_2O$ and melting at 50—60°; the anhydrous acid is hygroscopic, melts at 105—107°, when heated above its melting point forms a sublimate of *m*-nitrophenol, and when warmed with bromine water yields dibromo-*m*-nitrophenol (compare Willgerodt and Mohr, *Abstr.*, 1886, 1030). The sodium, $C_6H_3O_6NSNa_2$, sodium hydrogen, and barium, $C_6H_3O_6NSBa, H_2O$, salts are described.

The *m*-aminophenolsulphonic acid, formed by reduction of the above nitro-acid is probably identical with the acid obtained by direct sulphonation of *m*-aminophenolsulphonic acid (D.R.-P. 83447) and with Klappert's electrolytic reduction product (*Abstr.*, 1903, i, 85). The barium hydrogen salt, $(C_6H_6O_4NS)_2Ba, 4H_2O$, crystallises in brown needles and prisms. A comparative table of the properties of the known *m*-aminophenols is given.

p-Nitrophenol-*o*-sulphonic acid is obtained in a 45 per cent. yield by direct sulphonation of *p*-nitrophenol (Post, *Abstr.*, 1881, 92). The presence of catalytic agents such as mercury, boric acid, or infusorial earth, or the use of alkali polysulphates, influences the yield, but not the constitution, of the product. *p*-Nitrophenolsulphonic acid cannot be obtained by the action of chlorosulphonic acid on *p*-nitrophenol.

G. Y.

Reaction of an Oxydase Type exhibited by Halogen Derivatives of the Rare Earths. EUGÈNE FOUARD (*Compt. rend.*, 1906, 142, 1163—1165).—The accelerating action of the chlorides of the metals of the rare earths on the absorption of oxygen by quinol is much greater than the corresponding action of the chlorides of the alkali and alkaline earth metals (this vol., i, 421). The experiments were conducted by placing equal volumes of equivalent solutions of the metallic chlorides together with a definite quantity of a solution of

quinol into tubes, which were then sealed and placed in an oil-bath. After eight days the volume of oxygen present in the residual air was measured, and the ratio *R* between the volume of oxygen absorbed and the original volume of oxygen is given in the following table :

Solution of chloride.			Ratio <i>R</i> per cent.
Samarium	chloride	75·75 per cent.
Thorium	"	63·10 "
Cerium	"	57·71 "
Neodymium	"	54·23 "
Praseodymium	"	53·35 "
Lanthanum	"	22·60 "
Sodium	"	17·82 "

M. A. W.

Cholesterol. I. Addition of Hydrogen Chloride. JULIUS MAUTHNER (*Monatsh.*, 1906, 27, 305—314. Compare Mauthner and Suida, *Abstr.*, 1894, i, 486; 1903, i, 625; 1904, i, 49).—*Chlorocholestanol* (*cholesterol hydrochloride*), $C_{27}H_{45}OCl$, is formed together with β -dichlorocholestane by the action of hydrogen chloride on cholesterol dissolved in a mixture of ether and absolute alcohol cooled by ice; it crystallises from a mixture of chloroform and light petroleum in glistening, pliant, slender needles, melts and decomposes at 154—155°, does not form an additive compound with bromine, and when distilled loses hydrogen chloride, forming cholesterylene. It is decomposed by concentrated sulphuric acid, but is stable towards fuming nitric acid at the ordinary temperature, and when hydrolysed with alcoholic potassium hydroxide or acetate yields cholesterol, together with an oily product, probably an isomeride.

β -Dichlorocholestane, $C_{27}H_{44}Cl_2$, separates slowly from the ethereal-alcoholic filtrate from chlorocholestanol; it crystallises from a mixture of alcohol and benzene in flat needles, melts at 117°, and is stable towards fuming nitric acid, but is decomposed by concentrated sulphuric acid only slowly, forming a solution with slight green fluorescence. The β -dichloro-derivative is formed also by the action of hydrogen chloride on cholesteryl chloride, and is isomeric with cholestene dichloride (α -dichlorocholestane), previously described (Mauthner and Suida, *Abstr.*, 1894, i, 326).

Chlorocholestane, $C_{27}H_{45}Cl$, is formed by the action of hydrogen chloride on cholestene in chloroform solution; it crystallises in glistening, flat prisms or sheaves of iridescent leaflets, commences to sinter at 80°, melts at 91°, dissolves in boiling alcohol, and does not react with bromine in chloroform solution.

The above additive compounds of laevorotatory cholestene, cholesterol, and cholesteryl chloride are dextrorotatory. G. Y.

Cholesterol. VI. ADOLF WINDAUS (*Ber.*, 1906, 39, 2008—2014. Compare *Abstr.*, 1904, i, 49, 667, 1010; 1905, i, 128; this vol., i, 174; Diels and Abderhalden, this vol., i, 272).—The oxidation of cholestenone by potassium permanganate in neutral solution leads to the formation of (a) a small quantity of a *monobasic acid*, $C_{27}H_{44}O_4$,

which crystallises from dilute alcohol in long, thin needles and melts at 217—218°, and (b) a *keto-acid*, $C_{26}H_{42}O_3$, which crystallises from a mixture of benzene and light petroleum in tetragonal leaflets and melts at 155°. The *oxime*, $C_{26}H_{42}O_2 \cdot N \cdot OH$, crystallises in long, thin prisms and melts and decomposes at 191°. When brominated in glacial acetic acid solution, the keto-acid yields the *bromo-derivative*, $C_{26}H_{41}O_3Br$, which crystallises in needles, melts at 154—156°, and forms a *hydroxyketo-acid* when boiled with aqueous potassium hydroxide.

Oxidation of the keto-acid with bromine in aqueous potassium hydroxide leads to the formation of a hygroscopic *tricarboxylic acid*, $C_{26}H_{42}O_6$, which crystallises from benzene in stellate groups of needles, melts at 129—131°, and decomposes when more highly heated.

The author considers that the formation of the keto-acid from cholestenone shows that the latter cannot be an $\alpha\beta$ -unsaturated ketone.

G. Y.

Cholesterol. VII. ADOLF WINDAUS (*Ber.*, 1906, **39**, 2249—2262. Compare Abstr., 1904, i, 49, 667, 1010; 1905, i, 128; this vol., i, 174, and preceding abstract; van Oordt, *Inaug. Diss.*, 1901, Freiburg, i/B).—When a solution of cholesterol in a mixture of benzene and glacial acetic acid is oxidised by chromic acid, one of the products is an acid, $C_{27}H_{44}O_4$, which melts at 290°; its identity with the acid obtained by Diels and Abderhalden (Abstr., 1904, i, 880) as a product of the oxidation of cholesterol with potassium hypobromite was further indicated by its conversion into the monomethyl ester melting at 124°.

When oxycholestenone is heated at 180° for two hours with zinc dust, it is converted into cholestandione, identical with the product which the author had previously obtained from nitrocholesterol. A comparison of the formulæ for oxycholestenone, $C_{27}H_{40}O_2$, and for cholestandione, $C_{27}H_{42}O_2$, shows that in the reduction of the former by zinc dust a hydroxy-group had not been replaced by hydrogen, as would have been the case had oxycholestenone possessed a tertiary hydroxy-group; it is probable, on the other hand, that a simple addition of two hydrogen atoms had been effected. The conversion of oxycholestenone into cholestandione may be carried out quantitatively by reducing it with zinc and acetic acid at a lower temperature than 180°. The conclusion is accordingly drawn that oxycholestenone is an unsaturated diketone.

The presence of an enolic group in oxycholestenone is indicated by the formation of an ethyl ether and a benzyl ether. The ethyl ether is readily hydrolysed.

When oxycholestenone in ethereal solution is acted on by 20 per cent. potassium hydroxide, the yellow potassium salt of oxycholestenone separates and yields the characteristic phenylhydrazone. When this salt is allowed to remain under diminished pressure for several days, it undergoes transformation into a salt of an acid and no longer yields a hydrazone. This observation also supports the view that oxycholestenone contains an enolic group.

The dibromo-derivative of cholestandione is identical with the com-

pound obtained by the addition of bromine to oxycholestenone. By the further action of bromine, each is converted into *tribromocholestandione*, $C_{27}H_{39}O_2Br_3$, which separates from acetone in needles and melts at 195° . The two bromine atoms in oxycholestenone dibromide are probably in the 1 : 2-position.

It is highly probable that the keto-groups in cholestandione and oxycholestenone respectively are in the 1 : 4-position.

The *compound*, $C_{54}H_{85}O_3N(?)$, formed by heating cholestandione with alcoholic ammonia for six hours at 120° , separates from a mixture of chloroform and alcohol in needles which melt and decompose at over 300° .

The *compound*, $C_{27}H_{42}N_2$, formed by the action of hydrazine hydrate on cholestandione, separates from a mixture of benzene and methyl alcohol in tetragonal leaflets and softens at about 188° . In the formation of this compound, 1 mol. of the diketone interacts with 1 mol. of hydrazine with the elimination of 2 mols. of water.

The *compound*, $C_{27}H_{42}ON_2$, formed by the action of hydrazine hydrate on oxycholestenone, crystallises in yellow leaflets and melts at $160-161^\circ$.

The *compound*, $C_{33}H_{46}ON_2$, formed by the action of *o*-phenylenediamine on oxycholestenone, separates from ethyl acetate in brick-red leaflets and melts at $158-159^\circ$.

The *compound*, $C_{27}H_{42}O_6S(?)$, formed by the action of acetic anhydride and sulphuric acid on oxycholestenone, separates from benzene in needles and decomposes at about 148° .

The *compound*, $C_{29}H_{45}O_3N$, prepared by the action of hydroxylamine hydrochloride and sodium acetate on β -oxycholestenol acetate, separates from a mixture of benzene and light petroleum in needles and melts at $185-186^\circ$.

In cholesterilene, there is no system of conjugated double linkings. It is not acted on by sodium and ethyl (or amyl) alcohol.

Oxycholestenone is formed when cholesterilene is oxidised by chromic acid.

A. McK.

Synthesis of Aldehydes and Ketones from *as*-Disubstituted Ethylene Glycols and their Ethers. RICHARD STOERMER, E. (FREIHERR) SCHENCK ZU SCHWEINSBERG, FR. SIBBERN-SIBBERS, and P. RIEBEL (*Ber.*, 1906, **39**, 2288-2306).—*Diphenylphenoxymethylcarbinol*, $OH \cdot CPh_2 \cdot CH_2 \cdot OPh$, obtained in 71 per cent. yield by the interaction of magnesium phenyl bromide and ethyl phenoxyacetate, separates from alcohol in large, rhombic crystals and melts at 101° . When heated with alcoholic potash for twenty hours at 200° , it yields two products, diphenylethoxymethylcarbinol (compare Béhal and Sommelet, *Abstr.*, 1904, i, 222), which is identical with the synthetic ether obtained from magnesium phenyl bromide and ethyl ethoxyacetate, and diphenylethyleneglycol (compare Paal and Weidenkaff, this vol., i, 583), the *diacetate* of which melts at 145.5° . Both compounds are changed by boiling 20 per cent. sulphuric acid into diphenylacetaldehyde, the glycol completely, the ether to the extent of two-thirds. Dry diphenylethylene glycol is decomposed by

heating, yielding formaldehyde and benzhydrol, the latter being further changed into diphenylmethane and benzophenone.

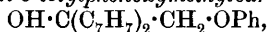
Benzoylcarbinol is conveniently obtained in good yield by digesting a cold alcoholic solution of bromoacetophenone with excess of potassium acetate; after a short heating on the water-bath, the hot liquid is poured into ice-cold water and the acetate thus obtained purified according to Fischer and Busch's directions (Abstr., 1891, 1514). Benzoylcarbinol reacts with magnesium phenyl bromide to form diphenylethylene glycol, according to the equation



In a similar way, diphenylphenoxyethylcarbinol is obtained from phenoxyacetophenone and magnesium phenyl bromide.

Phenoxydi-p-tolyloethylene, $\text{C}(\text{C}_7\text{H}_7)_2\cdot\text{CH}\cdot\text{OPh}$, is obtained when magnesium *p*-tolyl bromide (2 mols.) reacts with ethyl phenoxyacetate (1 mol.). It crystallises in colourless needles and melts at 122° . When heated for twelve hours at 240° with alcoholic potash, it yields di-*p*-tolylethylene and ethoxydi-*p*-tolylethylene; the latter is converted by hot 20 per cent. hydrochloric acid into *di-p-tolylacetaldehyde*, $\text{CH}(\text{C}_7\text{H}_7)_2\cdot\text{CHO}$, a colourless oil, which boils at 213° under 26 mm. pressure, reduces Fehling's and silver solutions, and forms an *oxime* crystallising in small, colourless needles and melting at 126.5° , and a *semicarbazone* which melts at 185° .

Magnesium *o*-tolyl bromide and ethyl phenoxyacetate react in the normal way, forming *di-o-tolylphenoxyethylcarbinol*,



which crystallises in colourless needles and melts at 130° .

Dimethylphenoxyethylcarbinol, $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OPh}$, obtained like the corresponding diphenyl compound, is a colourless oil with a sweet odour, which boils at 119° under 16 mm. and at 231° under the ordinary pressure, and forms a *phenylurethane* which melts at 70° . When heated with alcoholic potash at 200° , it yields dimethylethoxymethylcarbinol (compare Béhal and Sommelet, *loc. cit.*), which is converted by 20 per cent. sulphuric acid into *isobutaldehyde*.

Phenoxydimethyldiethylcarbinol, $\text{OPh}\cdot\text{CH}_2\cdot\text{C}(\text{Et})_2\cdot\text{OH}$, boils at $259\text{--}260^\circ$ and forms a *phenylurethane* which melts at 98° . Ethoxydimethyldiethylcarbinol yields diethylacetaldehyde by boiling with 20 per cent. sulphuric acid.

β -Phenylpropylene $\alpha\beta$ -glycol, $\text{OH}\cdot\text{CMePh}\cdot\text{CH}_2\cdot\text{OH}$, to the extent of 7.5, and its *anhydride*, $\text{CMePh}\langle\begin{smallmatrix} \text{CH}_2\cdot\text{O} \\ \text{O}\cdot\text{CH}_2 \end{smallmatrix}\rangle\text{CMePh}$, to the extent of 25 per cent., are obtained by the interaction of magnesium methyl iodide and benzoylcarbinol; they are separated by water, in which the former is easily soluble. The glycol forms colourless needles, melts at 44.5° , boils at $158\text{--}160^\circ$ under 25 mm. pressure, and is partially changed into hydratropaldehyde by 20 per cent. sulphuric acid. The anhydride, which is a yellow, odourless oil boiling at 194° under 15 mm. pressure, is not identical with Klages' oxide (Abstr., 1905, i, 523); it is converted by slightly acidified water at 180° into hydratropaldehyde.

β -Phenylbutylene $\alpha\beta$ -glycol, $\text{OH}\cdot\text{C}(\text{Et})\text{Ph}\cdot\text{CH}_2\cdot\text{OH}$, and its *anhydride*, $\text{C}_{20}\text{H}_{24}\text{O}_2$, are obtained from an ethereal solution of magnesium ethyl

iodide and benzoylcarbinol suspended in dry benzene, the relative yields depending on the order in which the one solution is added to the other. The former compound crystallises in needles, melts at 56° , and boils at $158\text{--}161^{\circ}$ under 20 mm. pressure; the latter is a viscous, yellow oil, which boils at $221\text{--}223^{\circ}$ under 20 mm. pressure, and is difficultly volatile in steam.

a-Phenylbutaldehyde, $\text{CHEtPh}\cdot\text{CHO}$, obtained from the preceding reaction products by slightly acidified water at 180° , is a colourless oil with a strong agreeable odour, which boils at $104\text{--}106^{\circ}$ under 15 mm. and at 211° under the ordinary pressure; the *oxime* is an oil, but the *semicarbazone*, best obtained from the sodium hydrogen sulphite compound, melts at 155° .

By the action of magnesium phenyl bromide on ethyl *a*-phenoxypropionate, the *phenyl ether* of $\beta\beta$ -diphenylpropylene- $\alpha\beta$ -glycol, $\text{OH}\cdot\text{CPh}_2\cdot\text{CHMe}\cdot\text{OPh}$, is obtained, which melts at 136° . Alcoholic potash at 220° converts it into an oil, from which $\beta\beta$ -diphenylpropylene

oxide, $\text{O}\begin{smallmatrix} \text{CHMe} \\ \diagup \\ \text{CPh}_2 \end{smallmatrix}$, was isolated, but not the corresponding ethyl ether in the pure state; the former melts at 67° , boils above 300° with slight decomposition, and forms an oily *chlorohydrin*, $\text{C}_{15}\text{H}_{15}\text{OCl}$.

aa-Diphenylpropylene $\alpha\beta$ -glycol, $\text{OH}\cdot\text{CPh}_2\cdot\text{CHMe}\cdot\text{OH}$, obtained from ethyl lactate by the Grignard method, crystallises in long needles and melts at 96.5° ; the *diacetate* melts at 153° .

Diphenylacetone, $\text{CHPh}_2\cdot\text{COMe}$, obtained quantitatively from the preceding glycol and slightly acidified water at 180° , is dimorphous, the one form melting at 46° , the other at 61° . The less fusible substance has not been transformed into its isomeride, but both yield the same *oxime*, which melts at 164.5° , *semicarbazone*, which melts at 170° , and *phenylhydrazone*, which melts at 131° .

$\beta\beta$ -Di-*p*-tolylpropylene $\alpha\beta$ -glycol, $\text{OH}\cdot\text{C}(\text{C}_7\text{H}_7)_2\cdot\text{CHMe}\cdot\text{OH}$, prepared in similar manner, melts at 67° , and when heated with acetic anhydride forms *di-p-tolylacetone*, $\text{CH}(\text{C}_7\text{H}_7)_2\cdot\text{COMe}$, which is also obtained by the direct distillation of the glycol; it boils at 194° under 20 mm. pressure. The *oxime* melts at 189° , the *semicarbazone* at 172° , and the *phenylhydrazone* at 122° . Di-*o*-tolylpropylene glycol is not obtained from magnesium *o*-tolyl bromide and ethyl lactate; when the reaction product is decomposed by ice and acetic acid, an oil is obtained from which a substance, apparently *o-tolualdehyde*, is obtained, together with *di-o-tolylacetone*, $\text{CH}(\text{C}_7\text{H}_7)_2\cdot\text{COMe}$, which is a viscous oil, boils at 198° under 12 mm. pressure, and does not form a sodium hydrogen sulphite compound. The *oxime* melts at 171° , the *semicarbazone* at 152° .
C. S.

Unsymmetrical Diphenylethylene Oxide and Diphenylethylene Glycol. CARL PAAL and ERICH WEIDENKAFF (*Ber.*, 1906, **39**, 2062—2063. Compare *Abstr.*, 1905, i, 436; this vol., i, 236).—*as*-Diphenylethylene oxide (Klages and Kessler, this vol., i, 498) may be obtained by the action of nitrous acid on diphenylaminomethylcarbinol. *as*-Diphenylethylene glycol, $\text{OH}\cdot\text{CPh}_2\cdot\text{CH}_2\cdot\text{OH}$, is readily prepared by the action of magnesium phenyl bromide on ethyl glycolate.

It crystallises from its aqueous solution in large, colourless needles, melting at 121° , and dissolves readily in most organic solvents.

J. J. S.

Optically Active 4-Methylcyclohexylidene-1-acetic Acid. WILLY MARCKWALD and RICHARD METH (*Ber.*, 1906, **39**, 2035—2038. Compare this vol., i, 360; Perkin and Pope, *Proc.*, 1906, **22**, 107).—The acid previously described readily loses carbon dioxide, yielding a hydrocarbon, C_8H_{14} , already described by Wallach, and its products of oxidation prove it to be 1-methyl-4-methylenecyclohexane. The constitution of the acid is therefore regarded as established.

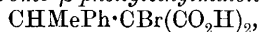
The cinchonine salt, when pure, melts at $62-64^{\circ}$, and has $[\alpha]_D + 16.0^{\circ}$.

J. J. S.

Simple Method for the Synthesis of α -Amino-acids. HANS BUCHERER (*Ber.*, 1906, **39**, 2033—2034).—Priority as against Zelinsky and Stadnikoff (this vol., i, 425) is claimed (compare *Abstr.*, 1905, i, 438).

J. J. S.

Phenylbutyric Acids and their α -Amino-derivatives. EMIL FISCHER and WILHELM SCHMITZ (*Ber.*, 1906, **39**, 2208—2215. Compare this vol., i, 182; Knoop and Hösli, *ibid.*, 431).—Chloroethylbenzene prepared by the action of chlorine on boiling ethylbenzene consists principally of the α -isomeride, as when boiled with copper nitrate solution it is oxidised to acetophenone, which is obtained in a yield of more than 60 per cent. of the theoretical. The following constitutions must therefore be ascribed to the derivatives of malonic and phenylbutyric acids previously described: *ethyl β -phenylethylmalonate*, $CHMePh \cdot CH(CO_2Et)_2$, instead of *ethyl γ -phenylethylmalonate*; *β -phenylethylmalonic acid*, $CHMePh \cdot CH(CO_2H)_2$, instead of *γ -phenylethylmalonic acid*; *α -bromo- β -phenylethylmalonic acid*,



instead of *α -bromo- γ -phenylethylmalonic acid*; and *α -bromo- β -phenylbutyric acid*, $CHMePh \cdot CHBr \cdot CO_2H$, and *α -amino- β -phenylbutyric acid*, $CHMePh \cdot CH(NH_2) \cdot CO_2H$, instead of *α -bromo- and α -amino- γ -phenylbutyric acids respectively*. The terms *prim.*-phenethyl and *sec.*-phenethyl are used by the authors for the groups $CHPh \cdot CH_2$ and $CHMePh$ respectively.

The following derivatives of γ -phenylethylmalonic and γ -phenylethylbutyric acids have been prepared from Grignard's ω -bromoethylbenzene (*Abstr.*, 1904, i, 213) in the same way as the β -phenyl compounds from α -chloroethylbenzene.

Ethyl γ -phenylethylmalonate, $CH_2Ph \cdot CH_2 \cdot CH(CO_2Et)_2$, is obtained as a colourless, viscid oil, which boils at $178-182^{\circ}$ under 16 mm. pressure. The *acid*, $CH_2Ph \cdot CH_2 \cdot CH(CO_2H)_2$, crystallises from benzene in microscopic needles, or from hot water in sheaves of small, colourless, pointed needles, melts and evolves carbon dioxide at $130-131^{\circ}$ (corr.), and when heated at 140° yields γ -phenylbutyric acid.

α -Bromo- γ -phenylethylmalonic acid, $CH_2Ph \cdot CH_2 \cdot CBr(CO_2H)_2$, crystallises from water in slender needles, melts and decomposes at 158°

(corr.), and when heated at 160—165° yields *α*-bromo-*γ*-phenylbutyric acid

, which is obtained as a viscid oil.

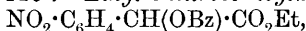
α-Amino-*γ*-phenylbutyric acid, prepared from the preceding bromo-acid, is identical with Knoop and Hössli's acid (*loc. cit.*). The *copper* salt forms a slightly blue, flocculent precipitate, which is only sparingly soluble in water.

β-Phenylbutyric acid, $\text{CHMePh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, formed by heating *β*-phenylethylmalonic acid above its melting point, crystallises from water in small needles, or from light petroleum in small prisms, melts at 38—39° (corr.), and distils at 160° under 16 mm. or at 270° under the ordinary pressure. It forms a *calcium* salt, which separates from its aqueous solution when heated as a viscid oil, redissolving as the solution cools. The *lead* salt forms a white, amorphous precipitate; the *silver* salt, $\text{C}_{10}\text{H}_{11}\text{O}_2\text{Ag}$, forms slender needles. G. Y.

Stereoisomeric Cinnamic Acids. WILLY MARCKWALD and RICHARD METH (*Ber.*, 1906, 39, 1966. Compare this vol., i, 360).—A reply to Erlenmeyer, jun., and Barkow (this vol., i, 429).

G. Y.

Derivatives of *o*-Nitromandelonitrile. GUSTAV HELLER and HEINRICH G. MAYER (*Ber.*, 1906, 39, 2334—2339).—*o*-Nitromandelonitrile forms an *acetyl* derivative which melts at 52° and a *benzoyl* derivative which melts at 90—91°; the *amide*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OBz})\cdot\text{CO}\cdot\text{NH}_2$, of the latter melts at 128°. *Ethyl o-nitrobenzoylmandelate*,



melts at 72°.

Benzoyldioxindole is obtained by reducing ethyl *o*-nitrobenzoylmandelate or the amide with stannous chloride and hydrochloric acid, and is identical with the substance obtained by benzoylating dioxindole (*Abstr.*, 1904, i, 416).

o-Nitrosobenzoic acid is the chief product formed when *o*-nitromandelonitrile is dissolved in alcoholic ammonia (compare *Ber.*, 1901, 34, 948); the *methyl* ester, obtained by the use of methyl sulphate and sodium carbonate, melts at 152—153°, and when reduced yields methyl anthranilate. C. S.

A New Step in the Reduction of the Nitro-group. GUSTAV HELLER (*Ber.*, 1906, 39, 2339—2346).—The first step in the reduction of the nitro-group is the formation of the group $\text{N}(\text{OH})_2$. When *o*-nitromandelonitrile, dissolved in 33 per cent. acetic acid, is cooled to 0° and treated with zinc dust, a *substance* is obtained which crystallises in quadratic plates or leaflets, decomposes at 145°, and reduces solutions of gold, silver, and platinum salts. From its composition and behaviour, the substance is regarded as a quinhydrone-like compound, composed of $\text{N}(\text{OH})_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CN}, \text{HCl}$ and $\text{OH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CN}, \text{HCl}$.

When heated on the water-bath with water and hydrochloric acid, about 40 per cent. of the substance is changed into *o*-nitrosomandelonitrile, $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CN}$, which crystallises in colourless needles with a faint blue shade, melts at 210°, and is converted by boiling dilute alkali hydroxides into anthroxanic acid. When warmed with ferrous sulphate and sodium hydroxide and then acidified, the substance

yields isatin, but if ammonia and ferrous sulphate are used, followed by sodium hydroxide, and the solution is then acidified and concentrated, isatyde is obtained.

When the quinhydrone compound is warmed with hydrochloric acid, the second of the components mentioned above yields isatin.

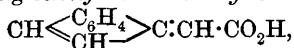
By acetylation, the substance yields isatin and 1-acetoxyisatin, $C_6H_4 \begin{smallmatrix} \text{N(OAc)} \\ \text{CO} \end{smallmatrix} \text{CO}$, which separates from benzene in orange-red plates, melts at 151—152°, gives the indophenin reaction, and by solution in an alkali hydroxide, followed by the addition of excess of hydrochloric acid, yields anthroxanic acid.

When 1-acetoxyisatin is treated with alcohol and phenylhydrazine, yellowish-green leaflets of 1-hydroxyisatinphenylhydrazone, $C_{14}H_{11}O_2N_3$, are obtained, which melt at 220°, but when it is warmed with excess of alcohol and phenylhydrazine, the osazone, $C_{20}H_{17}ON_5$, is formed, which crystallises in slender, yellow needles and melts at 169°. C. S.

Derivatives of Fulvene. II. Derivatives of Indeneoxalic Esters. JOHANNES THIELE and MAX RÜDIGER (*Annalen*, 1906, 347, 275—289. Compare this vol., i, 569; Thiele, *Abstr.*, 1900, i, 347; Wislicenus, *ibid.*, 346).—In accordance with the strong colour of indeneoxalic esters, these are represented as the enolic form, in which they are derivatives of the strongly coloured fulvene.

Methyl indeneoxalate, $CH \begin{smallmatrix} C_6H_4 \\ CH \end{smallmatrix} C:C(OH) \cdot CO_2Me$, formed with slight development of heat by the condensation of indene and methyl oxalate in presence of sodium ethoxide in absolute alcoholic solution, crystallises from benzene in orange-red needles and melts at about 90—92°, or at lower temperatures after repeated recrystallisation.

Ethyl α-hydroxyindeneacetate, $CH \begin{smallmatrix} C_6H_4 \\ CH \end{smallmatrix} CH \cdot CH(OH) \cdot CO_2Et$, prepared by reduction of ethyl indeneoxalate by means of aluminium amalgam and moist ether, is obtained as a yellow, viscid oil, which boils at 172° under 13 mm. pressure, and gives a deep red coloration with much concentrated sulphuric acid. It is readily hydrolysed by methyl-alcoholic or concentrated aqueous potassium hydrobromide, losing H_2O and forming *benzofulvenecarboxylic acid*,

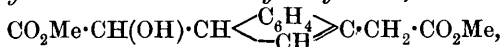


which crystallises from benzene in microscopic, orange leaflets, commences to sinter at 175°, and when more highly heated partially sublimes and finally decomposes. With alcoholic potassium hydroxide, it gives a violet-red coloration, becoming green and then yellow on addition of water, and yields methylinene when distilled with soda-lime, or in a vacuum, or in a current of hydrogen. The *methyl* ester, $C_{12}H_{10}O_2$, crystallises in yellow needles, melts at 62—63°, and resembles quinone in appearance.

Indeneacetic acid, $CH_2 \begin{smallmatrix} C_6H_4 \\ CH \end{smallmatrix} C \cdot CH_2 \cdot CO_2H$, prepared by reduction of benzofulvenecarboxylic acid by means of aluminium amalgam, or zinc dust and ammonia, or of methyl benzofulvenecarboxylate by means

of aluminium amalgam, crystallises in white needles, melts at 95—96°, remains unchanged when heated with 20 per cent. potassium hydroxide at 120° in a sealed tube, and yields methylindene when distilled with soda-lime. The *methyl ester*, $C_{12}H_{12}O_2$, is obtained as a yellow, viscid oil, which boils at 148—150° under 12 mm. pressure and solidifies partially when cooled by ice.

1-Oxaloindene-3-acetic acid, $CO_2H \cdot C(OH) : C \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} > C \cdot CH_2 \cdot CO_2H$, formed by hydrolysis of its esters, crystallises from dilute alcohol or acetic acid in orange-red needles, melts and decomposes at about 200°, and gives a brown to green coloration with ferric chloride. The *methyl hydrogen ester*, $CO_2Me \cdot C(OH) : C \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} > C \cdot CH_2 \cdot CO_2H$, prepared by the action of methyl oxalate on indeneacetic acid in presence of sodium methoxide in methyl-alcoholic solution, crystallises from chloroform in small, orange needles, or from a mixture of alcohol and chloroform in glistening leaflets, melts and decomposes at about 190°, and gives a transient, reddish-brown coloration with ferric chloride. The *dimethyl ester*, $C_{15}H_{14}O_5$, formed in the same manner from methyl indeneacetate and methyl oxalate, crystallises in yellow needles, melts at 109—110°, and gives with ferric chloride a similar coloration to the methyl hydrogen ester. When reduced with aluminium amalgam, it yields *dimethyl indene-1-acetate-3- α -hydroxyacetate*,

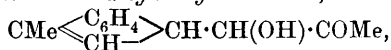


which is obtained as a yellow, viscid oil, giving a violet-red coloration with alcoholic potassium hydroxide.

Carboxybenzofulveneacetic acid, $CO_2H \cdot CH_2 \cdot C \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} > C : CH \cdot CO_2H$, is formed by hydrolysis of the preceding ester by means of alcoholic potassium hydroxide; it crystallises from toluene in small, light yellow needles, melts and decomposes at 240—250°, and is reduced by zinc dust and ammonia, forming a colourless acid (*indenediacetic acid*?).

1-Methylindene-3-oxalic acid, $CMe \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} > C : C(OH) \cdot CO_2H$, is obtained by hydrolysis of its ester; it crystallises in slender, yellow needles, darkens and decomposes at about 200°, and gives a reddish-brown to green coloration with alcoholic ferric chloride, becoming colourless on addition of water. The *ethyl ester*, $C_{14}H_{14}O_3$, prepared from methylindene and ethyl oxalate, crystallises in orange-red needles, melts at about 92—94°, decomposes slowly at the ordinary temperature, and couples with diazobenzenesulphonic acid in acid or alkaline solution. The *methyl ester*, formed from methyl oxalate and methylindene, crystallises in hard, orange needles, melts at 135—136°, gives a transient, brown coloration with ferric chloride, and couples with diazobenzenesulphonic acid.

Methyl 1-methylindene-3- α -hydroxyacetic acid,



formed by reduction of methyl methylindeneoxalate, is obtained as a

yellow, viscid oil, which decomposes when distilled, and gives with alcoholic potassium hydroxide a cherry-red, with concentrated sulphuric acid a red solution with green fluorescence.

1-Methylbenzofulvenecarboxylic acid, $\text{CMe} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} \text{C}:\text{CH}\cdot\text{CO}_2\text{H}$, prepared in the same way as benzofulvenecarboxylic acid, crystallises from benzene in orange needles and decomposes above 200° .

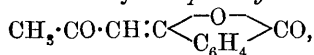
1-Methylindene-2-carboxylic acid, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \\ \text{CMe} \end{smallmatrix} \text{C}\cdot\text{CO}_2\text{H}$ (Roser, Abstr., 1888, 1303), forms a *methyl* ester, $\text{C}_{12}\text{H}_{12}\text{O}_2$, which crystallises in white needles and melts at 78° , and an *ethyl* ester, $\text{C}_{13}\text{H}_{14}\text{O}_2$, which forms needles and melts at 38° . G. Y.

Gabriel's Conversion of Phthalides into Indanediones. ALEXANDER FIBNER (*Ber.*, 1906, 39, 2202—2204. Compare Nathanson, Abstr., 1894, i, 37).—Quinolylacetophenone-*o*-carboxylic acid is converted into the red sodium derivative of quinophthalone by sodium ethoxide, not directly, but if first heated with alcohol and a small quantity of concentrated hydrochloric or sulphuric acid. The reaction takes place therefore between sodium ethoxide and *ethyl quinolylacetophenone-*o*-carboxylate*, $\text{C}_{20}\text{H}_{17}\text{O}_3\text{N}$. This crystallises from light petroleum in yellow needles and melts at 250° .

The conversion of *as*-quinophthalone into its sodium derivative by the action of alcoholic sodium ethoxide takes place in two stages: the first is marked by the formation of a golden-yellow solution; the second, in which the red colour of the sodium derivative appears, takes place slowly at the ordinary temperature, but quickly on heating. The intermediate product is probably the above ester or its sodium derivative. G. Y.

Transformations of Phthalylacetylacetone. CARL BÜLOW and MAX DESENISS (*Ber.*, 1906, 39, 2275—2281. Compare Abstr., 1904, i, 610; 1905, i, 42, 529).—Phthalylacetylacetone is decomposed into acetylacetone and phthalic acid by boiling water; into phthalamide and phthalimide by alcoholic ammonia, and into methylphthalimide by 30 per cent. methylamine at 100° . A solution of sodium hydroxide in the cold, of sodium carbonate or hydrogen carbonate when warmed, and of barium hydroxide when boiled, decomposes phthalylacetylacetone into phthalic acid and acetylacetone.

The reaction between phthalylacetylacetone and ten times its weight of concentrated sulphuric acid yields *phthalylacetone*,



which separates from alcohol in white, feathery crystals and melts at 183° .

Phthalylacetylacetone is transformed by sodium methoxide into 2-acetyl-1:3-diketohydrindene, and is decomposed by hydrazine yielding β -phthalylhydrazine; by semicarbazine yielding *phthalylsemicarbazide*, $\text{C}_9\text{H}_7\text{O}_3\text{N}_3$, which melts at 249° ; by *p*-nitrophenylhydrazine yielding *phthalyl-p-nitrophenylhydrazide*, $\text{C}_{14}\text{H}_9\text{O}_4\text{N}_3$, which melts at

247°. With hydroxylamine, the substance reacts normally, yielding *phthalylacetylacetone monoxime*, $C_{13}H_{11}O_4N$, which melts at 169°.

C. S.

Syntheses of Aromatic Aldehydes. I. LUDWIG GATTERMANN (*Annalen*, 1906, 347, 347—386. Compare Gattermann and Koch, *Abstr.*, 1897, i, 519; Gattermann and Frenzel, *Abstr.*, 1898, i, 476; Gattermann and Berchermann, *ibid.*, 581; Gattermann and Köbner, *Abstr.*, 1899, i, 363; Gattermann and Maffezzoli, *Abstr.*, 1904, i, 172).—The aldehydes described in this paper, which opens with a *résumé* of the author's three methods for the synthesis of aromatic aldehydes, have been prepared by the action of carbon monoxide and hydrogen chloride on hydrocarbons in presence of aluminium chloride and cuprous chloride.

Benzaldehyde is formed from benzene by this method only if aluminium bromide is substituted for the chloride. Dibenzylidenebenzidine melts at 234°, forming a liquid crystalline phase, changing to a clear liquid at 260°. The condensation products of other aromatic aldehydes with benzidine and substituted benzidines behave in the same manner.

When heated with concentrated hydriodic acid and red phosphorus in a sealed tube, *p*-tolualdehyde is reduced to *p*-xylene. Di-*p*-toluylidenebenzidine melts at 230°, forming a turbid liquid which becomes clear above the boiling point of sulphuric acid. Tolyldenaeazine melts at 158°; the phenylhydrazone melts at 112—113°. When reduced electrolytically in a mixture of glacial acetic acid and concentrated sulphuric acid with an *E.M.F.* of 5—6 volts and a current density of 1.2 amperes, *m*-nitro-*p*-tolualdehyde, which melts at 48—49° (43—44°; Hanzlik and Bianchi, *Abstr.*, 1899, i, 597), yields the

compound $COH \cdot C_6H_3Me \cdot N < \overset{O}{\underset{|}{CH}} \cdot C_6H_3Me \cdot NO_2$. This separates from benzene in yellow crystals, melts at 168°, and when oxidised with ferric chloride forms *nitroso-p-tolualdehyde*, $C_8H_7O_2N$, which crystallises in glistening, silvery needles and melts at 128°. 2:6-Dinitro-*p*-tolualdehyde, $C_8H_2Me(NO_2)_2 \cdot COH$, formed by the action of a mixture of fuming nitric and concentrated sulphuric acids on *p*-tolualdehyde, crystallises in yellow needles, melts at 109°, and forms 2:6-dinitro-*p*-toluic acid when oxidised with potassium permanganate.

3:5-Dinitro-4-methylbenzylidene chloride, $C_8H_6O_4N_2Cl_2$, formed by nitration of 4-methylbenzylidene chloride, crystallises in large, colourless needles, melts at 90°, and when hydrolysed by means of a mixture of fuming and concentrated sulphuric acids yields 2:6-dinitro-*p*-tolualdehyde.

Ethyl p-methylcinnamate, $C_{12}H_{14}O_2$, prepared by the action of ethyl acetate and sodium on *p*-tolualdehyde, is obtained as a colourless, strongly refracting oil, which boils at 278°, has an odour resembling that of ethyl cinnamate, and on hydrolysis yields *p*-methylcinnamic acid. The ester reacts with bromine in carbon disulphide solution, forming *ethyl αβ-dibromo-4-methyldihydrocinnamate*, $C_{12}H_{14}O_2Br_2$, which crystallises from alcohol in large, glistening prisms and melts at 76.5°, together with an oil, probably a stereoisomeride. *αβ*-Dibromo-

4-methylcinnamic acid melts at 192° (183° , Kröber, Abstr., 1890, 968). On treatment with potassium hydroxide in hot concentrated alcoholic solution, the preceding ester yields *bromo-4-methylcinnamic acid*, $C_{10}H_9O_2Br$, which crystallises from benzene in white needles and melts at 192° . If in the preparation of this acid the filtrate from the potassium bromide is boiled in a reflux apparatus, the product is *p-tolylpropionic acid*, $C_{10}H_8O_2$, which crystallises in long, colourless prisms, melts and decomposes at 148° , and when heated with aniline loses carbon dioxide, forming *p-tolylacetylene*.

m-Nitro-*p*-methylcinnamic acid melts at 173.5° (170 — 171° , Hanzlik and Bianchi, Abstr., 1899, i, 890).

p-Tolylideneacetone (Hanzlik and Bianchi, *loc. cit.*) distils at 142 — 145° under 15 mm. pressure as a strongly refracting oil. The *oxime*, $C_{11}H_{13}ON$, crystallises in colourless leaflets and melts at 126° . The *semicarbazone*, $C_{12}H_{15}ON_3$, forms colourless needles, becomes yellow on exposure to air, and melts at 202° . The *azine*, $C_{22}H_{24}N_2$, crystallises in yellow needles and melts at 190° . The phenylhydrazone forms yellow needles and melts at 154° (138° , Hanzlik and Bianchi, *loc. cit.*), and when heated above its melting point changes suddenly into *phenyl-p-tolylmethylpyrazoline*, $C_{17}H_{18}N_2$, which crystallises from light petroleum in colourless needles, melts at 112° , forms solutions with blue fluorescence, and gives Knorr's pyrazoline reaction. *m*-Nitro-*p*-tolylideneacetone is formed by nitration of *p*-tolylideneacetone.

Di-p-tolylideneacetone, $CO(CH:CH \cdot C_7H_7)_2$, is prepared by condensation of *p*-tolylideneacetone with *p*-tolualdehyde; it crystallises from alcohol in glistening, slightly yellow needles, melts at 175° , with 2 mols. of hydrogen chloride in ethereal solution forms an unstable scarlet *hydrochloride*, and yields an *additive* compound with ferric chloride and hydrogen chloride.

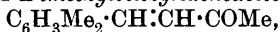
Di-p-methylbenzoin (Stierlin, Abstr., 1889, 513) crystallises in triclinic prisms [$a:b:c = 0.593:1:0.282$; $\alpha = 126^{\circ}51'44''$; $\beta = 116^{\circ}45'2''$; $\gamma = 76^{\circ}0'8''$].

Di-p-methylbenzilic acid, $C_{16}H_{16}O_3$, prepared by the action of aqueous potassium hydroxide on di-*p*-methylbenzil, crystallises in colourless needles, melts at 131° , and when heated at 150° forms an *anhydride*, $C_{32}H_{30}O_5$, which crystallises in colourless prisms and melts at 164° .

Hydro-p-toluamide, $N_2(CH \cdot C_7H_7)_3$, formed by the action of ammonia on *p*-tolualdehyde in cooled absolute alcoholic solution, crystallises in white needles, melts at 92° , and when heated at 130 — 140° for three to four hours, dissolved in alcohol, and treated with concentrated hydrochloric acid, is converted into *tri-p-methyl-amarine*, $C_{24}H_{24}N_2$. This crystallises from dilute acetone in colourless needles, melts at 127° , dissolves in alcohol, forming an alkaline solution, and becomes luminescent when heated with alcoholic potassium hydroxide at 70 — 75° in the dark. The *hydrochloride*, $C_{24}H_{25}N_2Cl$, crystallises in colourless needles and melts at about 295° . The *silver* derivative, $C_{24}H_{23}N_2Ag$, is formed as a white, amorphous precipitate. The *nitroso-derivative*, $C_{24}H_{23}ON_3$, forms yellow crystals and melts at 147° . When heated, hydro-*p*-toluamide yields ammonia, a polymeride of tolunitrile which melts above 260° , and trimethyl-lophine,

$C_{24}H_{22}N_2$. This crystallises from dilute alcohol in stout needles, melts at 234° , is a feeble base, and is more strongly luminescent than trimethylamarine when heated with alcoholic potassium hydroxide at 70° . The *acetate* crystallises in large octahedra, melts at 97° , and is decomposed by boiling alcohol.

3:4-Dimethylbenzaldehyde, $C_9H_{10}O$, formed from *o*-xylene, boils at 225° , and on oxidation yields 3:4-dimethylbenzoic acid. The *oxime*, $C_9H_{10}NOH$, crystallises from light petroleum in colourless needles and melts at 69° . The *azine*, $N_2(C_9H_{10})_2$, separates from alcohol in sulphur-yellow leaflets and melts at 132° . The *phenylhydrazone*, $C_{15}H_{16}N_2$, forms colourless, unstable crystals and melts at 96° . The *condensation* product with benzidine, $C_{30}H_{28}N_2$, crystallises in golden-yellow leaflets and melts at 158° to a turbid, at 250° to a clear, liquid. The *trithioaldehyde*, $C_{27}H_{30}S_3$, forms colourless crystals and melts at 147° . 3:4-Dimethylmandelic acid, $C_{13}H_{12}O_3$, crystallises in glistening, colourless leaflets and melts at 105° . 3:4-Dimethylcinnamic acid, $C_{11}H_{12}O_2$, is formed by acting with malonic acid on 3:4-dimethylbenzylidenaniline, and heating the product with hydrochloric acid; it crystallises in colourless needles and melts at 142° . The *ethyl ester*, $C_{13}H_{16}O_2$, formed by the action of ethyl acetate and sodium on 3:4-dimethylbenzaldehyde, is obtained as a colourless, strongly refracting, pleasant-smelling oil which boils at $180\text{--}185^\circ$ under 22 mm. pressure. 3:4-Dimethylbenzylideneacetone,



formed in the same way as tolylideneacetone, separates from ether in stout crystals, melts at 40° , and boils at 172° under 20 mm. pressure. The *semicarbazone*, $C_{13}H_{17}ON_3$, crystallises in colourless needles and melts at 207° .

2:4-Dimethylbenzaldehyde, formed from *m*-xylene, boils at $216\text{--}218^\circ$ (compare Bouveault, Abstr., 1896, i, 649). The *oxime*, $C_9H_{11}ON$, crystallises in strongly refracting prisms and melts at 88° . The *phenylhydrazone*, $C_{15}H_{16}N_2$, forms colourless leaflets and melts at 88° .

5-Nitro-2:4-dimethylbenzaldehyde, $C_9H_9O_3N$, forms yellow needles, melts at 81° , and on oxidation yields 5-nitro-2:4-dimethylbenzoic acid. 2:4-Dimethylmandelic acid, $C_{10}H_{12}O_3$, crystallises from benzene in colourless needles and melts at 119° . 2:4-Dimethylcinnamic acid, $C_{11}H_{12}O_2$, formed by the action of malonic acid and alcoholic ammonia on the aldehyde, crystallises in glistening, colourless needles and melts at 181° . When reduced with sodium amalgam it yields 2:4-dimethyldihydrocinnamic acid, $C_{11}H_{14}O_2$, which crystallises in glistening, colourless leaflets and melts at 108° . 2:4-Dimethylbenzylideneacetone, $C_{12}H_{14}O$, forms yellow crystals, melts at 32° , and boils at $145\text{--}148^\circ$ under 10 mm. pressure. The *semicarbazone*, $C_{13}H_{17}ON_3$, crystallises from alcohol in white needles and melts at 227° .

p-Xylene does not form an aldehyde, whilst 2:4:6-trimethylbenzaldehyde is formed from mesitylene in only small quantities by the carbon monoxide method.

2:4:5-Trimethylbenzaldehyde, formed from ψ -cumene, boils at 243° , is oxidised by potassium permanganate in dilute alkaline solution, forming durylic acid, and is reduced to durene by hydriodic acid and

red phosphorus. When exposed to direct sunlight, the colourless crystals of the aldehyde become yellow, changing again in the dark to the colourless state (compare Marckwald, Abstr., 1900, ii, 2). The *oxime*, $C_{10}H_{13}ON$, crystallises from light petroleum in colourless needles and melts at 102° . The *phenylhydrazone*, $C_{16}H_{18}N_2$, forms colourless leaflets and melts at 138° .

The nitration of ψ -cumylaldehyde, as also that of p -xylylaldehyde and of the corresponding acetophenones, leads to the formation of the *o*-nitro-derivatives as the main products, whilst the *m*-nitro-derivatives are formed at the same time in smaller amount.

o-Nitro- ψ -cumylaldehyde, $C_{10}H_{11}O_3N$, formed best at -5° to -10° , crystallises in almost colourless leaflets, melts at 142° , and yields hexamethylindigotin when heated gently with acetone and alcoholic potassium hydroxide. When reduced, it forms *o*-amino- ψ -cumylaldehyde, $C_{10}H_{13}ON$, which crystallises in yellowish-green leaflets, melts at 102 – 103° , and is volatile in a current of steam. When diazotised and boiled with dilute sulphuric acid, this yields *o*-hydroxy- ψ -cumylaldehyde, $C_{10}H_{12}O_2$, which crystallises from alcohol in colourless leaflets and melts at 78 – 79° .

o-Nitrodurylic acid, $C_{10}H_{11}O_4N$, formed by oxidation of the *o*-nitro-aldehyde with potassium permanganate, crystallises in colourless needles and melts at 192 – 193° . 6-Nitro-2:4:5-trimethylcinnamic acid, $C_{12}H_{13}O_4N$, formed by the action of sodium acetate and acetic anhydride on the *o*-nitro-aldehyde, crystallises from alcohol in slightly yellow leaflets and melts at 186 – 187° .

m-Nitro- ψ -cumylaldehyde, $C_{10}H_{11}O_3N$, crystallises from alcohol in long, colourless needles and melts at 128° . Dinitro- ψ -cumylaldehyde, $C_{10}H_{10}O_5N_2$, prepared by the action of potassium nitrate and concentrated sulphuric acid on the *o*-nitroaldehyde, crystallises from acetic acid in colourless needles and melts at 175° .

Cuminaldehyde is formed in good yield from cumene by the carbon monoxide method. The *azine*, $C_{20}H_{24}N_2$, crystallises in yellow needles and melts at 118° .

Diphenyl-4-aldehyde, $C_{13}H_{10}O$, prepared from diphenyl, crystallises from light petroleum, melts at 60 – 61° , and when oxidised by potassium permanganate yields diphenyl-4-carboxylic acid, which is reduced by hydriodic acid and red phosphorus, forming 4-methyldiphenyl. This crystallises in colourless leaflets and melts at 47 – 48° (Carnelly, this Journal, 1876, i, 13). The *oxime*, $C_{13}H_{10}NOH$, forms colourless needles and melts at 149 – 150° ; the *phenylhydrazone*, $C_{19}H_{16}N_2$, crystallises in slightly yellow needles and melts at 188 – 189° ; the *aniline* derivative, $C_6H_4Ph\cdot CH:NPh$, crystallises in colourless leaflets and melts at 150 – 151° .

Hydrindene-5-aldehyde, $CH_2\langle\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}\rangle C_6H_3\cdot CHO$, is formed in a 25 per cent. yield from hydrindene, together with an oil which has an odour of roses and boils at 168° under 18 mm. pressure, and a substance, $C_{17}H_{18}O$, which crystallises in colourless leaflets, melts at 83° , boils at 192° under 18 mm. pressure, is soluble in aqueous alkali hydroxides, and is precipitated from its alkaline solution by carbon dioxide.

The aldehyde forms a colourless oil which boils at 255 – 257° , and is

oxidised by potassium permanganate, forming trimellitic acid, or slowly by air, forming *hydrindene-5-carboxylic acid*, $C_{10}H_{10}O_2$. This crystallises in microscopic prisms and melts at 177° . The aldehyde forms an *oxime*, $C_{10}H_{11}ON$, crystallising in colourless leaflets and melting at 65° ; an *azine*, $C_{20}H_{20}N_2$, crystallising in yellow needles and melting at 162° ; and an *aniline* derivative, $C_{16}H_{15}N$, crystallising in stellate aggregates of needles and melting at 85° . G. Y.

A New Reaction of Aldehydes. Action of *iso*Hydroxycarbamide on Benzaldehyde, and Properties of Benzylidene-carbamidoxime. Action of Water on Benzylidenecarbamidoxime. A. CONDUCHE (Bull. Soc. chim., 1906, [iii], 35, 418—430 and 431—435).—Most of the data given in the first paper have been recorded already (Abstr., 1905, i, 288). The products of the action of hydrochloric acid on benzylidenecarbamidoxime are now given as benzonitrile and ammonium chloride (compare *loc. cit.*). It is also found that the product of the action of alcoholic or aqueous alkalis on benzylidenecarbamidoxime is α -benzaloxime, and not the β -isomeride as previously supposed (*loc. cit.*). Potassium cyanate condenses immediately with β -benzaloxime hydrochloride to form benzylidene-carbamidoxime. The same condensation product is formed when potassium cyanate reacts with α -benzaloxime, but only in presence of nitric acid (compare *loc. cit.*).

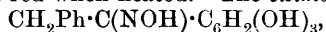
In the second paper it is shown that when benzylidenecarbamidoxime is boiled with water or when heated in closed tubes with water at 120° or at 160 — 220° the same products are formed, namely, α -benzaloxime, benzamide, benzonitrile, and carbamide, the relative proportions of these substances formed depending on the temperature employed.

T. A. H.

Action of Nitrogen Tetroxide on Benzaloxime. GIACOMO PONZIO (J. pr. Chem., 1906, [ii], 73, 494—496. Compare Beckmann, Abstr., 1889, 980; Scholl, Abstr., 1891, 315).—The action of 1 mol. of nitrogen tetroxide on 1 mol. of benzaloxime in ethereal solution leads to the formation of benzaloxime peroxide and diphenylglyoxime peroxide in yields of 15 per cent., and of phenyldinitromethane in a yield of 50 per cent. of the theoretical, whilst the action of 2 mols. of nitrogen tetroxide leads to the formation of phenyldinitromethane in a yield of 75 per cent. of the benzaloxime, no peroxide being formed.

G. Y.

Phenylacetic Acid. Ketone Dyes. Trihydroxydeoxybenzoin and its Derivatives. EMILIO NOELTING and VIKTOR KADIERA (Ber., 1906, 39, 2056—2060).—*Phenylgallacetophenone* (*trihydroxydeoxybenzoin*), $CH_2Ph \cdot CO \cdot C_6H_2(OH)_3$, obtained by heating together phenylacetic acid, pyrogallol, and zinc chloride at 150° for thirty minutes, crystallises from water, in which it is somewhat sparingly soluble, as pale yellow prisms melting at 141 — 142° . It dissolves readily in most organic solvents and in dilute potassium hydroxide, giving a yellow solution which turns red when heated. The *oxime*,



crystallises in pale yellow needles melting at 166° . It dissolves sparingly in chloroform, and its solutions in alkali hydroxides are first yellow, but rapidly turn green. The isomeric *isonitroso*-derivative, $\text{OH}\cdot\text{N}:\text{CPh}\cdot\text{CO}\cdot\text{C}_6\text{H}_2(\text{OH})_3$, obtained by the action of nitrous acid on the ketone, crystallises from dilute alcohol in bright yellow cubes melting at 144° and soluble in hot water and most organic solvents.

The *diisonitroso*-derivative, $\text{OH}\cdot\text{N}:\text{CPh}\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}_6\text{H}_2(\text{OH})_3$, forms colourless crystals melting at 168° and dissolves readily in alcohol or glacial acetic acid; when boiled with dilute hydrochloric acid, it yields *trihydroxybenzil*, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_6\text{H}_2(\text{OH})_3$, which crystallises from hot water in colourless needles melting at 143° and readily soluble in most solvents. J. J. S.

1:4-Anthraquinone. CARL LIEBERMANN (*Ber.*, 1906, 39, 2089—2090).—A reply to Lagodzinski (this vol., i, 439). C. S.

The Products of the Action at a High Temperature of Sodium *iso*Butoxide or Propoxide on Camphor. ALBIN HALLER and JULES MINGUIN (*Compt. rend.*, 1906, 142, 1309—1313. Compare

Abstr., 1892, 72).—*iso*Butylcamphol, $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CH}\cdot\text{CH}_2\cdot\text{CHMe}_2 \\ | \\ \text{CH}\cdot\text{OH} \end{smallmatrix}$, ob-

tained by heating sodium *isobutoxide* and camphor in an autoclave at 220 — 230° for twenty-four hours, forms opaque, white crystals, distils between 235° and 255° , melts at 55° , and has $[\alpha]_D + 20.7^{\circ}$ in alcoholic solution; the *acetate* boils at 135° under 20 mm. pressure. *iso*Butylcam-

phor, $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CH}\cdot\text{CH}_2\cdot\text{CHMe}_2 \\ | \\ \text{CO} \end{smallmatrix}$, obtained by oxidising *isobutylcamphol*

by means of potassium permanganate, melts at 28° , and has $[\alpha]_D + 72.4^{\circ}$ in alcoholic solution. When heated with bromine in sealed tubes at 100°

it yields *isobutylidenecamphor*, $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{C}\cdot\text{CH}\cdot\text{CHMe}_2 \\ | \\ \text{CO} \end{smallmatrix}$, an oily liquid

which boils at 145° under 10 mm. pressure, has $[\alpha]_D + 114.4^{\circ}$, and yields *isobutyric* and *camphoric* acids on oxidation. The *nitrosate*,

$\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{C}\cdot\text{C}_4\text{H}_8\text{O}_4\text{N}_2 \\ | \\ \text{CO} \end{smallmatrix}$, formed by the action of concentrated nitric

acid or amyl nitrite and nitric acid, forms thin, white needles, melts with decomposition at 178° , is slightly soluble in alcohol and ether, more readily so in boiling benzene or acetone, and has $[\alpha]_D + 93^{\circ}$. By the action of dilute potassium hydroxide it is converted into *isonitroso-*

hydroxyisobutylcamphor, $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{C}(\text{OH})\cdot\text{C}(\text{C}_3\text{H}_7)\cdot\text{NOH} \\ | \\ \text{CO} \end{smallmatrix}$, which crystal-

lises from a mixture of ether and light petroleum in the form of thin, white needles melting at 95° .

Propylcamphol, $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CHPr}^a \\ | \\ \text{CH}\cdot\text{OH} \end{smallmatrix}$, prepared in similar manner to the corresponding *isobutyl* compound, crystallises from methyl alcohol, melts at 61° , and has $[\alpha]_D + 12.5^{\circ}$; the *acetate* boils at 120° under 10 mm. pressure and solidifies at 0° . *Propylcamphor*, $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CHPr}^a \\ | \\ \text{CO} \end{smallmatrix}$, is a liquid which

boils at 123° under 14 mm. pressure and has $[\alpha]_D + 55.6^\circ$. *Propylidene-camphor*, $C_8H_{14} \begin{smallmatrix} C:CH \cdot CH_2Me \\ \diagdown \\ CO \end{smallmatrix}$, is a liquid which has $[\alpha]_D + 87^\circ$ and has not yet been obtained quite pure, but which yields the *nitrosate*, $C_8H_{14} \begin{smallmatrix} C:C_3H_6O_4N_2 \\ \diagdown \\ CO \end{smallmatrix}$, melting and decomposing at 160°.

M. A. W.

Carvone. III. The Semicarbazones of Carvone. HANS RUPE and KARL DORSCHKY (*Ber.*, 1906, **39**, 2112—2115. Compare Abstr., 1905, i, 449; this vol., i, 374).—The carvone semicarbazone melting at 141—142° (Knoevenagel and Samel, this vol., i, 296) was obtained two years ago by the authors by adding to a concentrated aqueous solution of semicarbazide hydrochloride, carvone, alcohol, and finally potassium acetate, rise of temperature being carefully avoided; without this precaution and by using sodium hydrogen carbonate in the place of potassium acetate, the semicarbazone which melts at 162—163° (Baeyer, Abstr., 1894, i, 535) is obtained. Both forms are crystallographically identical and mutually convertible, the former changing completely into the latter by prolonged boiling in methyl-alcoholic solution or by careful heating at 170—175°; the latter isomeride is only partially converted into the former in boiling methyl alcohol, the complete transformation being observed only once in the case of a specimen which had been kept for a year. The two isomerides are soluble in the ordinary organic solvents, sparingly in the cold, easily on warming.

The isomeride with the higher melting point is unchanged in pyridine solution; the other changes sufficiently slowly to enable its rotatory power to be measured. The former has $[\alpha]_D 11.50^\circ$ and the latter 11.30° at 20°. The specific rotation of the latter is constant for a short time, and then suddenly changes to another constant value about five minutes smaller.

[With WALTER HOTZ.]—The semicarbazones are monoclinic $[a:b:c = 0.50550:1:0.4706; \beta = 83^\circ 26']$. C. S.

Aroma of Natural Musk. HEINRICH WALBAUM (*J. pr. Chem.*, 1906, [ii], **73**, 488—493).—When distilled with steam, crude musk yields 1.4 per cent. of a dark brown oil, about half of which distils at 200—210° under 9 mm. pressure.

Muskone, $C_{15}H_{28}O$ or $C_{16}H_{30}O$, is obtained by treating the distillate with alcoholic potassium hydroxide and distilling the product at 160—164° under 7 mm. pressure. It is a colourless, viscid oil, which has a strong but pleasant odour of musk, boils at 142—143° under 2 mm., or with slight decomposition at 327—330° under 752 mm. pressure, has a sp. gr. 0.9268 at 15°, $n_D 1.479$ at 25° or 1.4844 at 15°, and $[\alpha]_D - 10.6'$. It is only sparingly soluble in water, but readily so in alcohol, does not form an additive compound with sodium hydrogen sulphite, and does not give a red coloration with rosaniline decolorised by sulphur dioxide.

The *oxime* crystallises in needles and melts at 46°. The *semi-*

*carbazon*e, $C_{16}H_3ON_3$ or $C_{17}H_{33}ON_3$, crystallises in slender, white prisms, melts at $133-134^\circ$, and is odourless, but gives an odour of musk when heated with dilute sulphuric acid. Muskone is not identical with Bauer's ketone musk (Abstr., 1898, i, 523).

The fraction boiling at $65-106^\circ$ under 7 mm. pressure, obtained in the purification of muskone, has an unpleasant odour and gives the pine-wood reaction for pyrrole.

G. Y.

Copaiba Balsam from Surinam. LEOPOLD VAN ITALLIE and C. H. NIEUWLAND (*Arch. Pharm.*, 1906, **244**, 161-164. Compare Abstr., 1904, i, 1037).—The bulk of the resin is soluble in 5 per cent. aqueous sodium carbonate; the resin-acid has an acid number 171 and saponification number 178, and cannot be crystallised or separated into different acids by fractional precipitation of its salts. The *resen* cannot be crystallised.

From the sesquiterpene alcohol, which melts at $114-115^\circ$ when purified, a *sesquiterpene* was obtained, of which the molecular weight corresponds with the formula $C_{15}H_{24}$; it is a mobile liquid which boils at 252° under 759 mm. pressure, has a sp. gr., 0.952 at 15° , n_D 1.5189 at 15° , and $[\alpha]_D -61.7^\circ$; in the air, it soon changes to a resinous solid.

C. F. B.

Formula of Elaterin. ARMAND BERG (*Bull. Soc. chim.*, 1906, [iii], **35**, 435-437. Compare Abstr., 1898, ii, 447).—Elaterin has the formula $C_{28}H_{38}O_7$, yields a *diacetyl* derivative, and on hydrolysis with potassium hydroxide in alcohol furnishes acetic acid (1 mol.) and *elateridin*. The latter, by the further action of the alkali, yields *elateric acid*. These products are all amorphous and non-volatile.

T. A. H.

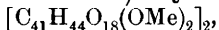
Curcumin. C. LORING JACKSON and LATHAM CLARKE (*Ber.*, 1906, **39**, 2269-2270. Compare Abstr., 1905, i, 804).—As a result of Zeisel determinations with curcumin, it is concluded that the formula for curcumin is $C_{14}H_{14}O_4$, and not $C_{21}H_{20}O_6$, that assigned to it by Ciamician and Silber.

A. McK.

Condensation of Gallocyanin Dyes with Aminosulphonic Acids. EUGENE GRANDMOUGIN (*Zeit. Farb. Ind.*, 1906, **5**, 201).—Gallocyanin dyes condense with aminosulphonic acids, when warmed with them in aqueous suspension, to form dyes which are bluer in colour than the original substances; the condensation of prune (Sandoz) with sulphanilic acid is described in detail. Naphthionic acid, *o*-toluidinesulphonic acid, *p*-toluidinesulphonic acid, and $\beta\beta$ -naphthyl-aminesulphonic acid can be used in place of sulphanilic acid, but dimethylmetanilic acid does not condense with the dyes, a free aminoradicle apparently being essential for the condensation.

W. A. D.

Tannins. EDUARD STRAUSS and BERNHARD GSCHWENDNER (*Zeit. angew. Chem.*, 1906, **19**, 1121-1125).—*Quebracho tannin*,



was obtained from the bark of *Quebracho colorada* by extracting first with chloroform and then with alcohol. On adding water to the

alcoholic extract and warming, phlobaphens are deposited from the solution, which are then removed by shaking the solution with Tripoli powder. On concentrating the solution in a vacuum, the tannin was precipitated by means of lead acetate, the lead salt after filtration being then suspended in water and decomposed with hydrogen sulphide. The aqueous solution so obtained was then evaporated in a vacuum, and the residue taken up in the least amount of alcohol and poured into absolute ether. By this means, the tannin was obtained in the form of light flakes which were rapidly dried in a vacuum over sulphuric acid and phosphoric oxide; it at once becomes sticky on exposure to moist air. Analyses agreed with the formula $C_{43}H_{50}O_{20}$, which is the formula given by Schuett to the tannin from quinine.

By heating the tannin with a mixture of acetic anhydride and glacial acetic acid, an *acetyl* derivative is obtained, which, however, has the formula $(C_{30}H_{22}O_{11}Ac_6)_2$, forms a white powder which is fairly readily soluble in alcohol, very soluble in acetone, ethyl acetate, glacial acetic acid, or acetic anhydride, but is insoluble in water, ether, or benzene. The corresponding *benzoyl* derivative, $(C_{30}H_{22}O_{11}Bz_6)_2$, is a white solid; it darkens at 200° and decomposes at 215° . An aqueous solution of the tannin allowed to remain for two days with a solution of formaldehyde deposited a dark red substance which could not be further purified. When reduced with sodium amalgam, the tannin yields a compound of the formula $(C_{30}H_{28}O_{11})_2$.

Maletto tannin, $(C_{43}H_{50}O_{20})_2$, was obtained from finely-powdered Maletto bark by extraction with 96 per cent. alcohol. From its analysis and properties it appears to be identical with Quebracho tannin.

Tannin from tea, $(C_9H_{10}O_5)_x$, was obtained from finely-powdered black tea by first extracting it with chloroform and then with alcohol, and proceeding with the extraction and purification already described. It forms an almost white powder. If lead acetate is used in the purification, a compound of the formula $C_{13}H_{19}O_{10}$ is obtained.

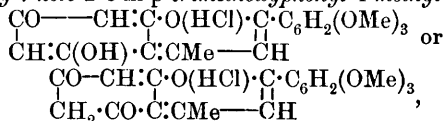
Sumach tannin, $(C_{16}H_{15}O_{11})_x$, was prepared according to Loewe's instructions. A determination of methoxyl showed that the formula should be $C_{32}H_{29}O_{11} \cdot OMe$. P. H.

Iodotannin. VIGNERON (*J. Pharm. Chim.*, 1906, [vi], 23, 469—471).—A two per cent. solution of tannin in water to which one per cent. of iodine has been added gives a brown precipitate with sodium hydrogen carbonate, a red coloration with potassium cyanide, a red coloration, slight precipitate, and free iodine on addition of nitric acid containing nitrous acid, and when this is followed by potassium cyanide, the red coloration changes to yellow, and a thick, white precipitate is formed.

A similar solution of iodogallic acid gives a black precipitate with sodium hydrogen carbonate, and no precipitate on the addition of nitric acid containing nitrous acid, and followed by potassium cyanide. The reaction with potassium cyanide alone is similar to that with the iodotannin solution. The author is of opinion that iodotannin extracts recently sold in France for making galenical preparations are prepared from gallic acid and not from tannin. T. A. H.

Formation of Methronic Acid. GEORG SCHROETER (*Ber.*, 1906, 39, 2129—2131).—A claim for priority and a criticism of Trephilleff's views regarding the mechanism of the formation of methronic acid (this vol., i, 528).
A. McK.

Quinonoid Benzopyran Derivatives. CARL BÜLOW and CARL SCHMID (*Ber.*, 1906, 39, 2027—2033. Compare this vol., i, 201, 300).—Phloroglucinol condenses with 2:3:4-trimethoxybenzoylacetone in the presence of hydrogen chloride in acetic acid solution, yielding 5-hydroxy-7-keto-2-o-m-p-trimethoxyphenyl-4-methyl-1:4-benzopyran hydrochloride,

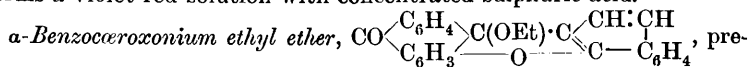


which crystallises from alcohol containing a small amount of hydrogen chloride in long, dark yellow needles containing $1\text{H}_2\text{O}$. The salt is partially hydrolysed in aqueous solution, and melts and decomposes at $218\text{--}219^\circ$. The *sulphate*, $\text{C}_{19}\text{H}_{18}\text{O}_6 \cdot \text{H}_2\text{SO}_4 \cdot \text{C}_2\text{H}_6\text{O}$, melts at $216\text{--}217^\circ$; the alcohol of crystallisation is removed by prolonged heating at 100° . When crystallised from alcohol containing 25 per cent. of sulphuric acid, a *sulphate*, $\text{C}_{19}\text{H}_{18}\text{O}_6 \cdot 2\text{H}_2\text{SO}_4$, which crystallises in orange needles melting at $155\text{--}156^\circ$, is obtained. The *picrate*, $\text{C}_{25}\text{H}_{21}\text{O}_{13}\text{N}_3$, forms orange needles, changes colour at 100° , and melts and decomposes at $219\text{--}220^\circ$. The *base*, $\text{C}_{19}\text{H}_{18}\text{O}_6 \cdot \text{H}_2\text{O}$, forms small, brownish-red needles, softens at $140\text{--}145^\circ$, and is insoluble in ether and only sparingly soluble in benzene. It cannot be acetylated, but yields an *oxime*, $\text{C}_{19}\text{H}_{19}\text{O}_6\text{N}$, melting at $132\text{--}136^\circ$, and a *phenylhydrazone*, $\text{C}_{31}\text{H}_{30}\text{O}_4\text{N}_4$, which crystallises from alcohol in plates and melts at $113\text{--}114^\circ$.

When the hydrochloride is heated with concentrated hydrochloric acid at $150\text{--}180^\circ$, it yields 5-hydroxy-7-keto-2-o-m-p-trihydroxyphenyl-4-methyl-1:4-benzopyran hydrochloride, $\text{C}_{16}\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O} \cdot \text{HCl}$, in the form of flesh-red, flat needles melting at 288° . The corresponding *base*, $\text{C}_{16}\text{H}_{12}\text{O}_6$, crystallises in dark brown, slender needles with a green lustre; it does not melt below 300° , and is insoluble in ether or benzene.
J. J. S.

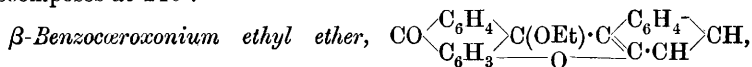
Benzocæroxonium Compounds. EDUARD LAUBE (*Ber.*, 1906, 39, 2245—2249).—*Erythroxyanthraquinone α-naphthol ether* [*1-α-naphthoxyanthraquinone*], $\text{C}_{24}\text{H}_{14}\text{O}_3$, prepared by heating a mixture of potassium anthraquinone-1-sulphonate and potassium α-naphthoxide for eight hours at $150\text{--}160^\circ$, separates from light petroleum in yellow crystals and melts at $275\text{--}276^\circ$. When warmed with concentrated sulphuric acid, it forms a purple solution.

1-β-Naphthoxyanthraquinone, prepared in an analogous manner, forms a violet-red solution with concentrated sulphuric acid.



pared by heating 1-α-naphthoxyanthraquinone with 70 per cent. sulphuric acid at 150° , separates from alcohol in colourless leaflets and

melts at 197—198°. The *ferrichloride*, $C_{24}H_{13}O_2Cl, FeCl_3$, of the base decomposes at 240°.



melts at 193—194°. The *ferrichloride* of the corresponding base melts at 240°.

Acetyl- α -benzoceroxonol, $C_{26}H_{16}O_3$, prepared by reducing benzoceroxonium salts by zinc dust and glacial acetic acid and then acetylating the product, separates from alcohol in yellow crystals. *Acetyl- β -benzoceroxonol* is brownish-yellow and melts at 195—200°.

By further reducing the benzoceroxonol compounds with hydriodic acid a small amount of *benzoceroxene* is obtained with other products.

A. McK.

Aconitine and Aconine from Aconitum Napellus. HEINRICH SCHULZE (*Arch. Pharm.*, 1906, **244**, 136—159, 165—196).—The first seventeen pages contain an historical account of previous researches. The results of the present research have already been published in part (*Abstr.*, 1905, i, 656).

Purified aconitine, melting at 197—198° and identical in crystalline form with that analysed by Dunstan and Ince (*Trans.*, 1891, 278—281), was found to have a composition corresponding, not with the formula proposed by these investigators or with that of Wright, but with those proposed by Freund and Beck, $C_{34}H_{47}O_{11}N$ or $C_{34}H_{45}O_{11}N$ (*Abstr.*, 1894, i, 263). The hydrobromide was obtained crystallised from a mixture of alcohol and ether with $\frac{1}{2}H_2O$, when it melted and decomposed at 206—207°, and also crystallised with $2\frac{1}{2}H_2O$; the α -aurichloride, melting at 136.5°, crystallised with $3H_2O$. Aconitine is best hydrolysed by heating with water in an autoclave under 6—7 atmospheres pressure; the yield of aconine hydrochloride was 85 per cent. of the theoretical.

The tetra-acetyl derivative of picroaconitine (benzoylaconine) is not different from the triacetyl derivative of aconitine (acetylbenzoylaconine), as Dunstan and Carr thought (*Trans.*, 1895, 461, 462); the two substances melt at 207—208° and are identical. Aconine does not form a quaternary ammonium salt with methyl iodide or sulphate, or an amino-oxide with hydrogen peroxide. Aconine hydrochloride and hydrobromide, melting at 175—176° and 225°, were obtained crystallised with 2 and $1\frac{1}{2}H_2O$ respectively.

When aconitine is heated with methyl alcohol at 120—130°, the acetyl group is eliminated as acetic acid, but instead of picroaconitine *methylpicroaconitine* is obtained; the *hydrobromide* and *hydrochloride* of this crystallise each with $3H_2O$ and melt at 188—189° and 190° respectively; the base, which also is crystalline, is hydrolysed to aconine, benzoic acid, and methyl alcohol when it is heated with a large excess of water at 150—160° for twenty-four hours, the hydrolysis taking place much less readily than in the case of aconitine, where heating for six hours suffices. When aconitine is heated with ethyl alcohol, ethylpicroaconitine is formed, but in worse yield than methylpicroaconitine.

Aconine hydrobromide crystallises with $1\frac{1}{2}\text{H}_2\text{O}$, and melts and decomposes at about 225° . With bromine, the alkaloid forms a perbromide, but no addition or substitution product. Neither aconine nor aconitine, nor the tetra-acetyl derivative of the latter, decolorises potassium permanganate rapidly in dilute sulphuric acid solutions.

Alkaline permanganate or chromic acid oxidises aconine with formation of aldehyde, and, in the latter case, of methylamine. In the former case, the main product was amorphous. In the latter case, the main product, which was both acid and basic, could not be obtained crystalline; a portion had basic properties, and from this a crystalline hydrochloride, $\text{C}_{24}\text{H}_{85}\text{O}_8\text{N}\cdot\text{HCl}$ (or $\text{C}_{24}\text{H}_{37}\text{O}_3\text{N}\cdot\text{HCl}$), with $3\text{H}_2\text{O}$, melting at 213° , was obtained. C. F. B.

Old Decomposed Cocaine Hydrochloride. PIERRE BRETEAU (*J. Pharm. Chim.*, 1906, [vi], 23, 474—476).—In a sample, obviously decomposed, of this alkaloidal salt made in 1891, methyl benzoate, benzoic acid, and ecgonine hydrochloride were found. The decomposition is attributed to the presence of a small quantity of water in the original salt. T. A. H.

Derivatives of Caffeine and Reactions of its Glyoxaline Nucleus. BRISSEMORET (*Bull. Soc. chim.*, 1906, [iii], 35, 316—321).—When a mixture of caffeine and salicylic acid in molecular proportions is dissolved in boiling water, there separates on cooling colourless, acicular crystals of the compound $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\cdot\text{C}_7\text{H}_6\text{O}_3$. An analogous product is obtained with protocathechuic or gallic acid.

Similar compounds may be obtained of 3:7-dimethylxanthine and gallic and salicylic acids and of 1:3-dimethylxanthine and gallic acid.

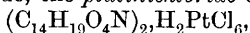
All these compounds dissolve on adding sodium hydroxide to their suspensions in water, and the bases may be then either filtered out or dissolved out by an appropriate solvent. It is possible to determine their composition by this means. The author regards the formation of these compounds as due to the influence of the glyoxaline ring in caffeine, and as evidence for the accuracy of this view points out that similar combinations may be brought about between glyoxaline itself and gallic or salicylic acid and that each of these may be isolated in a crystalline condition by mixing a solution of the base in ether with a like solution of the appropriate acid. T. A. H.

Behaviour of Cotarnine towards Grignard's Reagent. MARTIN FREUND and HANS HERMANN REITZ (*Ber.*, 1906, 39, 2219—2237. Compare Abstr., 1904, i, 187).—1-Ethylhydro-

cotarnine, $\text{CH}_2\begin{matrix} \diagup \text{O}\cdot\text{C}\cdot\text{C}(\text{OMe})\cdot\text{C}\cdot\text{CHEt}\cdot\text{NMe} \\ \diagdown \text{O}\cdot\text{C}\cdot\text{CH}—\text{C}\cdot\text{CH}_2—\text{CH}_2 \end{matrix}$, prepared by the

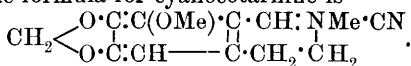
action of magnesium ethyl iodide on cotarnine, separates from dilute alcohol in rhombic pyramids and melts at $59\text{--}60^\circ$. Its hydrochloride crystallises in needles and melts at $215\text{--}216^\circ$; its dichromate crystallises in rhombic plates, whilst its methiodide separates from alcohol in hexagonal plates and melts at $188\text{--}189^\circ$. The 5-bromo derivative, $\text{C}_{14}\text{H}_{18}\text{O}_3\text{NBr}$, separates from light petroleum in octagonal plates and melts at 104° ; the orientation of the bromine atom as indicated is correct, since the same compound is formed when

magnesium ethyl iodide acts on bromocotarnine. When α -ethylcotarnine is oxidised with hydrogen peroxide, it is converted into the corresponding amino-oxide, the *platinichloride* of which,

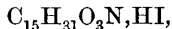


forms tetragonal plates and melts at 196—197°.

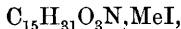
Attempts to prepare methoxyl derivatives of benzyl α -hydrocotarnine by the action of magnesium alkyl halides on cyanocotarnine failed; when magnesium ethyl iodide, for example, acts on cyanocotarnine, ethyl hydrocotarnine is produced, a result which indicates that the probable formula for cyanocotarnine is



1-Propylhydrocotarnine, $\text{C}_{15}\text{H}_{21}\text{O}_3\text{N}$, prepared by the action of magnesium propyl iodide on cotarnine, separates from light petroleum in tetragonal pyramids and melts at 66—67°. Its *hydriodide*,



forms rhombic plates and melts at 165—166°. Its *methiodide*,

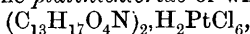


separates from alcohol in tetragonal crystals and melts at 165—166°.

1-isoPropylhydrocotarnine *hydriodide*, $\text{C}_{15}\text{H}_{31}\text{O}_3\text{N}, \text{HI}$, separates from alcohol in rhombic plates and melts at 196—197°. α -isoPropylhydrocotarnine *methiodide* separates from alcohol in needles and melts at 144—145°.

1-isoButylhydrocotarnine, $\text{C}_{16}\text{H}_{23}\text{O}_3\text{N}$, separates from light petroleum in tetragonal pyramids and melts at 46—47°. Its *hydrochloride* separates from water in octagonal crystals and melts at 217—218°; its *platinichloride* melts and decomposes at 208—209°; its *hydrobromide* melts at 205—206°; its *methiodide* separates from alcohol in hexagonal plates and melts at 189—190°.

When 1-methylhydrocotarnine is oxidised by hydrogen peroxide, it forms an amino-oxide, the *platinichloride* of which,



crystallises from dilute alcohol in plates and melts at 198°, whilst the corresponding *hydriodide* melts at 116°.

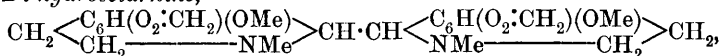
1-Phenylhydrocotarnine, $\text{C}_{18}\text{H}_{19}\text{O}_3\text{N}$, prepared from magnesium phenyl iodide and cotarnine cyanide, separates from light petroleum in pyramids and melts at 97—98°. It may also be prepared from cotarnine hydrochloride and magnesium phenyl iodide.

1-p-Methoxyphenylhydrocotarnine, $\text{C}_{19}\text{H}_{21}\text{O}_4\text{N}$, is a viscid oil.

1- α -Naphthylhydrocotarnine, $\text{C}_{22}\text{H}_{21}\text{O}_3\text{N}$, melts at 120—122°; its *hydrobromide* separates from dilute alcohol in cubes and melts at 253°.

1-Benzylhydrocotarnine, $\text{C}_{19}\text{H}_{21}\text{O}_3\text{N}$, separates from light petroleum in rhombic plates and melts at 70°. Its *hydriodide* separates from alcohol in plates and melts at 217—218°.

Di-hydrocotarnine,



prepared by the action of magnesium acetylene tetrabromide on cotarnine, crystallises from water in rhombohedra and melts at 163—164°. The *hydrobromide*, $\text{C}_{24}\text{H}_{28}\text{O}_6\text{N}_2, 2\text{HBr}, 2\text{H}_2\text{O}$, crystallises

from water in rhombic needles and, when dehydrated, melts at 233—234°; the *hydrochloride*, $C_{24}H_{28}O_6N_2 \cdot 2HCl \cdot 2H_2O$, separates from water in silky, rhombic leaflets and melts at 231—232°; the *hydriodide*, $C_{24}H_{28}O_6N_2 \cdot 2HI$, separates from alcohol in needles and melts at 234—235°. The *hydrogen sulphate*, $C_{24}H_{28}O_6N_2 \cdot 2H_2SO_4 \cdot 2H_2O$, crystallises from water in pyramids and melts and decomposes at 236—237°; the *methiodide*, $C_{24}H_{28}O_6N_2 \cdot MeI$, crystallises from water in needles and melts at 233—234°.

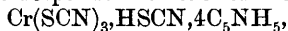
Di-hydrocotarnine may also be obtained by the action on cotarnine of the magnesium compounds of alkyl iodides, methylene chloride, benzylidene chloride, ethylene bromide, and piperonyl chloride respectively.

p-Cyanobenzyl iodide, prepared by the action of potassium iodide on *p*-cyanobenzyl chloride, separates from alcohol in needles and melts at 143—144°. It does not form a magnesium compound.

The physiological action of a number of the compounds described has been tested.
A. MCK.

Conversion of Ephedrine into ψ -Ephedrine. ERNST SCHMIDT (*Arch. Pharm.*, 1906, 244, 239—240. Compare Abstr., 1904, i, 769).—A much better yield of ψ -ephedrine is obtained by heating ephedrine hydrochloride with ten times its weight of 25 per cent. hydrochloric acid for twelve hours in the water-bath. Even then the conversion is not complete; it seems that equilibrium is reached between the two substances.
C. F. B.

Tetrathiocyanodipyridinechromium Salts. PAUL PFEIFFER and W. OSANN (*Ber.*, 1906, 39, 2115—2125).—*Pyridinium tetrathiocyanodipyridinechromiates*.—When dry potassium or ammonium chromothiocyanate is heated on the water-bath with anhydrous pyridine for four hours, a *substance* is obtained which separates from a small quantity of hot pyridine in glistening, dark red, prismatic crystals, stable in the air; it corresponds with the formula

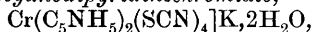


but does not give a coloration with ferric chloride. At 100° it loses 1 mol. C_5NH_5 , yielding a *substance*, $Cr(SCN)_3 \cdot HSCN \cdot 3C_5NH_5$, which again takes up 1 mol. C_5H_5N by crystallisation from this solvent. Sand and Burger's formula (this vol., i, 487) is rejected, and arguments are advanced in favour of regarding the substance



as the normal additive compound of 1 mol. C_5H_5N and the acid $[Cr(C_5NH_5)_2(SCN)_4]H$; the substance $Cr(SCN)_3 \cdot HSCN \cdot 4C_5NH_5$ is regarded as belonging to the class of the anomalous ammonium salts (compare Werner, Abstr., 1903, i, 234). When either of the compounds suspended in cold water is treated with chlorine, a *dihydroxylochloride*, $[Cr(C_5NH_5)_2(OH)_2(OH)_2]Cl$, is obtained; potassium hydroxide eliminates the pyridine, and by subsequent treatment with concentrated hydrochloric acid pure tetra-aquodipyridinechromium chloride is obtained.

Potassium tetrathiocyanodipyridinechromiate,

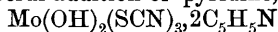


is the chief product of the reaction between anhydrous pyridine and potassium chromothiocyanate; after crystallisation from hot water, it is obtained as a stable, red powder. It can also be crystallised from aniline or quinoline, does not react with ferric chloride, and is decomposed by chlorine in the presence of cold water with the formation, ultimately, of tetra-aquodipyridinechromium chloride. When the dried substance is crystallised from pyridine, an additive compound, $[\text{Cr}(\text{C}_5\text{NH}_5)_2(\text{SCN})_4]\text{K}, 4\text{C}_5\text{NH}_5$, is obtained in the form of transparent, red crystals, which quickly effloresce in air, but not in an atmosphere of pyridine. Sodium chromothiocyanate yields similar compounds, $[\text{Cr}(\text{C}_5\text{NH}_5)_2(\text{SCN})_4]\text{Na}, 3\text{H}_2\text{O}$ and $[\text{Cr}(\text{C}_5\text{NH}_5)_2(\text{SCN})_4]\text{Na}, 4\text{C}_5\text{NH}_5$.

The $4\text{C}_5\text{NH}_5$ in these additive compounds is regarded as being in combination with the alkali metal (compare Rosenheim and Löwenstamm, *Abstr.*, 1903, i, 325). C. S.

Halogen Compounds of Molybdenum and Tungsten. II.

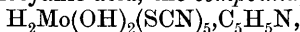
ARTHUR ROSENHEIM and MORDUCH KOSS (*Zeit. anorg. Chem.*, 1906, 49, 148—156. Compare *Abstr.*, 1905, ii, 717; Weinland and Knoll, *Abstr.*, 1905, ii, 323; Sand and Burger, *Abstr.*, 1905, i, 923; Hofmann and von der Heide, *Abstr.*, 1896, ii, 605).—When molybdenum trioxide, MoO_3 , is added in excess to a 10 per cent. aqueous solution of thiocyanic acid and the mixture boiled and filtered, a deep red solution is obtained, from which, on the careful addition of pyridine,



can be isolated in the form of brownish-red needles. It is thus shown that, contrary to the generally accepted view, sexavalent molybdenum can be reduced to the quinquevalent state by boiling with thiocyanic acid alone. The corresponding *quinoline* compound,



prepared in an analogous manner, crystallises from absolute alcohol in dark, reddish-brown needles. From a solution of the pyridine compound in excess of thiocyanic acid, the compound,

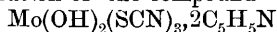


was obtained in black, lustrous, rhombic crystals, readily decomposed by water.

When either of the pyridine compounds is boiled with concentrated hydrogen chloride until all the thiocyanic acid is driven off, dipyridine-pentachloromolybdate, $\text{H}_2\text{MoCl}_5, 2\text{C}_5\text{H}_5\text{N}$, is obtained in light green needles. The three *bromides*, $\text{H}_2\text{Mo}(\text{OH})_2\text{Br}_5, 2\text{C}_5\text{H}_5\text{N}, 2\text{H}_2\text{O}$, $\text{HMo}(\text{OH})_2\text{Br}_4, \text{C}_5\text{H}_5\text{N}$, and $\text{H}_2\text{Mo}(\text{OH})_2\text{Br}_5, 2\text{C}_9\text{H}_7\text{N}$, recently described by Weinland and Knoll (*loc. cit.*), were also prepared and analysed; the formulæ ascribed to them differ slightly from those found by their discoverers.

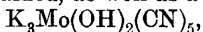
Concentrated hydriodic acid exerts a reducing action on both the pyridine and quinoline compounds; from the respective solutions the compounds $\text{H}_5\text{Mo}_2\text{I}_{13}, 5\text{C}_5\text{H}_5\text{N}$ and $\text{H}_3\text{Mo}_2\text{OI}_9, 3\text{C}_9\text{H}_7\text{N}$, containing quadrivalent molybdenum, were isolated in the form of black, lustrous needles.

From an aqueous solution of the compound



and excess of potassium cyanide, a compound, $\text{K}_5\text{Mo}(\text{OH})_2(\text{CN})_8$, was

obtained in yellow plates. With a large excess of potassium cyanide, the compounds $K_4MoO_2(CN)_4 \cdot 10H_2O$, in violet-red crystals, and $K_4MoO_2(CN)_4 \cdot 5H_2O$, already described by Hofmann and von der Heide (*loc. cit.*), were obtained, as well as a new compound,



which forms deep blue needles.

G. S.

Quinoline Hydrochloride. Action of Acid Chlorides on Quinoline. OSKAR ECKSTEIN (*Ber.*, 1906, 39, 2135—2138).—Quinoline hydrochloride, prepared by the action of benzoyl chloride or of acetyl chloride on quinoline in the presence of traces of water, has the formula $(C_9NH_7 \cdot HCl)_2 \cdot H_2O$, the melting point of which agrees with that recorded in the literature, namely, 94° ; *anhydrous quinoline hydrochloride*, however, melts at 134° , whilst its *platinichloride* forms prisms and melts at 227.5° . Its *hydrogen chloride additive compound*, $(C_9NH_7 \cdot HCl)_2 \cdot HCl$, prepared by passing a current of dry hydrogen chloride into an ethereal solution of quinoline, melts at 82° .

In Einhorn and Holland's acylation method, whereby the acylation of a given compound is conducted by the action of an acid chloride on its solution in a tertiary base, the assumption that an additive compound is formed from the acid chloride and the tertiary base has been adduced by Einhorn and others. The author describes the additive compounds which acetyl chloride and benzoyl chloride respectively form with quinoline.

The compound, $C_9NH_7 \cdot AcCl$, prepared by allowing a dry ethereal solution of quinoline and acetyl chloride to remain at a low temperature for a considerable time, forms colourless crystals, is unstable and deliquescent, being readily decomposed into quinoline and acetyl chloride.

The compound, $C_9NH_7 \cdot BzCl$, prepared in an analogous manner, boils at 105° under 12 mm. pressure, is hygroscopic, and assumes a dark red tint on exposure to air. When acted on by water it forms benzoic anhydride, benzoyl chloride, quinoline, and quinoline hydrochloride.

A. McK.

Kynurine Ethers. HANS MEYER (*Monatsh.*, 1906, 27, 255—266). Compare this vol., i, 108; Wenzel, *Abstr.*, 1895, i, 70).—The action of sodium methoxide on 4-chloroquinoline in methyl-alcoholic solution at the ordinary temperature for seventeen days, or at 130° for one

hour, leads to the formation of 4-methoxyquinoline, $C_6H_4 \begin{smallmatrix} C(OMe):CH \\ \diagup \quad \diagdown \\ N = CH \end{smallmatrix}$,

which solidifies in a freezing mixture, melts at 31° , commences to boil at 245° , and on continued distillation is converted partially into the ψ -methyl ether, the mixture boiling above 360° . The methoxyquinoline is soluble in ether but insoluble in water. The *mercurichloride*, $C_{10}H_9ON \cdot HHgCl_3$, crystallises in long, white needles, melts and decomposes at 188 — 190° , and is stable towards light; the *platini-chloride* forms almost colourless, delicate, glistening scales, and melts and decomposes at 227 — 228° ; the *aurichloride*, $C_{10}H_9ON \cdot HAuCl_4$, forms small, lemon-yellow crystals and melts and decomposes at 196 — 197° .

When heated at 300—310°, 4-methoxyquinoline is converted completely into the ψ -methyl ether, $C_6H_4 \begin{smallmatrix} \text{CO} \text{---} \text{CH} \\ \diagdown \quad | \\ \text{NMe} \cdot \text{CH} \end{smallmatrix}$, which, when crystallised from water, melts at about 90° and loses water at 110°; the anhydrous substance melts at 143° and is soluble in water or benzene, but is insoluble in ether. When evaporated with hydrochloric acid, it is converted into *kynurine methochloride*, which crystallises in delicate needles and melts at about 178°. The *aurichloride* forms small, light yellow needles and melts at 168—170°; the *platinichloride* crystallises in orange-yellow needles and melts and decomposes at 212°; the crystalline *mercurichloride* melts at 178°.

Wenzel's ethylkynurine (*loc. cit.*) is 4-ethoxyquinoline and not the ψ -ethyl ether, as it yields ethyl iodide, although slowly, when boiled with hydriodic acid of sp. gr. 1.7. When heated at about 360°, it changes into the ψ -ethyl ether, $C_6H_4 \begin{smallmatrix} \text{CO} \text{---} \text{CH} \\ \diagdown \quad | \\ \text{NEt} \cdot \text{CH} \end{smallmatrix}$, which was isolated as the *aurichloride*. This crystallises in sheaves of lemon-yellow needles and melts and decomposes at 155°.

G. Y.

Quinaldinic [Quinoline-2-carboxylic] Acid. EMIL BESTHORN and JOS. IBELE (*Ber.*, 1906, 39, 2329—2334. Compare Abstr., 1905, i, 612; Meyer, *ibid.*, i, 155, 666).—Quinoline-2-carboxylic acid, prepared by Koenigs' method (Abstr., 1899, i, 389), melts and decomposes at 156°. The authors have repeated the preparation of the chloride and have again obtained the substance melting at 97—98° by using freshly prepared thionyl chloride; if recovered thionyl chloride is employed, the reaction follows another course (compare Meyer, *loc. cit.*). The methyl ester melts at 85° and the amide at 132—133°.

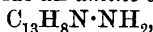
When quinoline-2-carboxylic acid is nitrated at 60—70° with concentrated sulphuric and nitric acids, a mixture of two mononitro-compounds is obtained, which is separated by means of their barium salts. 5-Nitroquinoline-2-carboxylic acid melts and decomposes at 203°, the 8-nitro-compound at 177°. The constitutions are determined by heating them above their melting points, when carbon dioxide is evolved and 5-nitro- and 8-nitro-quinoline respectively are obtained.

C. S.

Nitro- and Amino-derivatives of α -Naphthaquinoline and their Oxidation to Quinoline-7:8-dicarboxylic Acid. RUDOLF HAID (*Monatsh.*, 1906, 27, 315—340).—The two nitro-derivatives of α -naphthaquinoline described by Claus and Imhoff (Abstr., 1898, i, 333) were mixtures. On repeating the nitration under the same conditions and fractionally crystallising the product from alcohol and benzene, the author obtained four nitro- α -naphthaquinolines. Two of these, melting at 175° and 230° respectively, and constituting together 90 per cent. of the product, have the nitro-group in position 7, 8, 9, or 10, as on reduction and oxidation both yield quinoline-7:8-dicarboxylic acid.

Nitro- α -naphthaquinoline, $C_{13}H_8N \cdot NO_2$, melting at 230°, crystallises in glistening, yellow needles, or in aggregates of transparent plates which change slowly into the yellow needles. The *hydrochloride*

crystallises in white needles and melts at $245\text{--}250^\circ$; the *nitrate*, $\text{C}_{13}\text{H}_8\text{O}_2\text{N}_2\cdot\text{HNO}_3$, forms slightly yellow, strongly refracting needles or stout prisms and melts at 220° ; the *sulphate* crystallises in glistening needles and melts at 243° . When reduced with stannous chloride and hydrochloric acid, it yields an *amino- α -naphthaquinoline*,



which crystallises from alcohol in thin, colourless, transparent, brittle leaflets or rhombic plates and melts at 151° . The *hydrochloride* forms white prisms, commences to decompose at 215° , and dissolves in water, forming a blood-red solution which has an acid reaction.

Nitro- α -naphthaquinoline, $\text{C}_{13}\text{H}_8\text{O}_2\text{N}_2$, melting at 175° , crystallises from alcohol in spherical aggregates of long, thin, yellow, glistening needles. The *hydrochloride* crystallises in yellow prisms and melts and decomposes at $220\text{--}221^\circ$; the *nitrate* forms long needles and melts and decomposes at 193° . When reduced with stannous chloride and hydrochloric acid, the nitro-compound yields an *amino- α -naphthaquinoline*, which crystallises in aggregates of yellow leaflets and melts at 175° ; the *hydrochloride* crystallises in long, white, silky needles and commences to decompose at 230° .

Nitro- α -naphthaquinoline, melting at 166° , crystallises from alcohol in white needles or leaflets. The *hydrochloride* forms long, delicate, white needles and loses hydrogen chloride above 100° ; the *nitrate* forms yellow needles, commences to decompose at 125° , and is melted at 150° .

Nitro- α -naphthaquinoline, melting at 155° , crystallises in long, yellow, glistening needles and is readily soluble in alcohol or benzene. The *hydrochloride* forms yellow, strongly refracting needles and melts and decomposes at $210\text{--}211^\circ$; the *nitrate* forms yellow, strongly refracting needles and melts at 178° .

Quinoline-7:8-dicarboxylic acid, $\text{C}_{11}\text{H}_7\text{O}_4\text{N}\cdot\text{H}_2\text{O}$, prepared by the oxidation of the above amino- α -naphthaquinolines with dilute potassium permanganate in dilute sulphuric acid solution cooled by ice, crystallises in stellate aggregates of microscopic prisms, melts and decomposes at $206\text{--}207^\circ$, and yields an odour of quinoline when sublimed. The *hydrochloride* crystallises in long prisms and melts and decomposes at 212° ; the *sodium hydrogen* ($+3\text{H}_2\text{O}$), *acid copper*, *normal copper* ($+\frac{1}{2}\text{H}_2\text{O}$), *nickel*, *lead*, and *silver* salts are described.

The amine melting at 175° yields on oxidation, together with quinoline-7:8-dicarboxylic acid, an amorphous product which is probably α -phenylpyridinedicarboxylic acid. G. Y.

Quinonaphthalone. ALEXANDER EIBNER and M. LÖBERING (*Ber.*, 1906, 39, 2215—2218. Compare Eibner, *Abstr.*, 1904, i, 1049).—*s*-Quinonaphthalone, $\text{C}_{22}\text{H}_{13}\text{O}_2\text{N}$, prepared by heating 1:8-naphthalic anhydride with 2-methylquinoline and zinc chloride at 210° , forms long, matted, greenish-yellow needles, melts at 261° , is readily soluble in chloroform or glacial acetic acid, and forms traces of an unstable, dark red compound with aniline. The *sodium* derivative, $\text{C}_{22}\text{H}_{12}\text{O}_2\text{NNa}$, crystallises from alcohol in sheaves of yellowish-red needles and is decomposed by dilute mineral acids or much water. The action of bromine on quinonaphthalone in chloroform solution at $50\text{--}60^\circ$ leads

to the formation of a *perbromide*, $C_{22}H_{12}O_2NBr_4$, which crystallises in small, glistening, orange-yellow leaflets, melts and loses bromine at 239° , decomposes when recrystallised from chloroform, and yields quinonaphthalone when treated with alcohol, water, or ammonia. The *perbromide*, $C_{22}H_{12}O_2NBr_6$, formed by the action of an excess of bromine on quinonaphthalone in cold chloroform solution, crystallises in long, matted, yellowish-brown needles, and when heated with water yields a *monobromo-derivative*, which crystallises in white leaflets, becomes yellow, and yields quinonaphthalone when recrystallised (compare Eibner and Merkel, Abstr., 1902, i, 494).

as-Quinonaphthaline, $C_{22}H_{14}ON_2$, prepared by heating naphthalimide with 2-methylquinoline and zinc chloride at 180° , crystallises in long, orange-red needles, melts at 235° , is only sparingly soluble in alcohol, ether, or light petroleum, and with bromine in chloroform solution forms a *bromo-derivative*, which crystallises in light brown needles and forms a blood-red precipitate with diazonium chloride in sodium hydroxide solution.

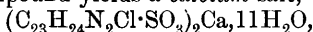
as-Quinophthalone, *as-quinophthaline*, and *as-quinonaphthaline* decolorise potassium permanganate rapidly in cold acetone solution, whereas *s-quinophthalone* and *s-quinonaphthalone* give a red coloration with potassium permanganate, which is decolorised only on prolonged heating. The action of the *s-* as also of the *as-* compounds on potassium permanganate is accelerated by the presence of sodium carbonate.

G. Y.

Influence of Nuclear Substituents on the Shade of Malachite-green. EMILIO NOELTING and PAUL GERLINGER (*Ber.*, 1906, 39, 2041—2053).—E. and O. Fischer have already shown that a nitro-substituent in the para position produces a yellower shade of green, but in the ortho-position a bluer shade, and that it is practically without effect in the meta-position. Similar generalisations hold good with respect to methyl, chlorine, and methoxyl, chlorine producing the greatest effect and methoxyl the least. *p'p''-Tetramethyldiamino-o'''-methyltriphenylmethane*, $C_6H_3Me \cdot CH(C_6H_3 \cdot NMe_2)_2$, is most readily prepared (95 per cent. yield) by condensing *o*-tolualdehyde with dimethylaniline, and may also be obtained, although not in a crystalline form, by eliminating the amino-group from the condensation product of Michler's hydrol and *m*-toluidine, or by the action of phosphorus oxychloride on *o*-toluic acid and dimethylaniline. It crystallises from alcohol in glistening needles, melts at $102-103^\circ$, and when oxidised with lead peroxide and hydrochloric acid yields a dye, the *additive* compound of which, with zinc chloride, forms green crystals with a bronze lustre and yields blue solutions. The sulphonic acid of the leuco-compound yields a *barium* salt, $(C_{24}H_{27}O_3N_2S)_2Ba \cdot 8H_2O$, in the form of soft, glistening plates, which readily turn green on exposure to the air.

The corresponding *p'p''-tetramethyldiamino-m'''-methyltriphenylmethane*, obtained from *m*-tolualdehyde, crystallises from alcohol in colourless needles and melts at $84-85^\circ$. When oxidised, it yields a copper-red dye, but the aqueous solutions are bluish-green and so impart a blue colour to fabrics. The *p'''-methyl* derivative (Hanzlik and Bianchi,

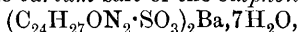
Abstr., 1899, i, 597) yields an oxidation product which dyes yellowish-green. The leuco-compound yields a *sulphonic acid*, the *sodium* salt of which, $C_{24}H_{27}N_2 \cdot SO_3Na, 2\frac{1}{2}H_2O$, when oxidised yields a dye which imparts the same colour to a fabric as the non-sulphonated dye. The 2:3:6-trimethyl derivative, $C_6H_2Me_3 \cdot CH(C_6H_4 \cdot NMe_2)_2$, prepared by eliminating the amino-group from aminotetramethyldiaminotrimethyltriphenylmethane (Abstr., 1892, 187), has not been obtained in a crystalline form. When oxidised it yields a dark red dye which dissolves in water to a blue solution. *o'''*-Chloro-*p''*-tetramethyldiaminotriphenylmethane crystallises from alcohol or toluene in glistening needles, melts at 145—146°, and on oxidation yields Geigy's setocyanin. The zincchloride dyes a greenish-blue. The *sulphonic acid* of the leuco-compound yields a *calcium* salt,



which crystallises from water in glistening needles. When oxidised it yields a product which dyes blue.

The *m'''*-chloro-derivative, when crystallised from alcohol mixed with a little zinc dust, forms colourless needles, melts at 112°, and dissolves readily in most organic solvents. The *p'''*-chloro-derivative melts at 98—99°, and not at 142—143° as stated by Kaeswurm (Abstr., 1886, 552).

p''-Tetramethyldiamino-*o'''*-methoxytriphenylmethane, obtained by condensing dimethylaniline and the methyl ether of salicylaldehyde with alcoholic hydrochloric acid, crystallises from alcohol in glistening needles, melts at 146°, and is only sparingly soluble in ether. The *sodium* salt of the *sulphonic acid* crystallises in glistening plates, and the *ammonium* salt, $C_{24}H_{27}ON_2 \cdot SO_3NH_4, H_2O$, in slender needles. The *m'''*-methoxyleuco~~malachite~~-green forms glistening plates melting at 123° and is fairly readily soluble in alcohol or ether. The isomeric *p'''*-methoxy-compound melts at 105° and dissolves readily in most organic solvents. The *barium* salt of the *sulphonic acid*,



and the *sodium* salt, $C_{24}H_{27}ON_2 \cdot SO_3Na, 8H_2O$, have been analysed.

A small amount of *p''p'''*-tetramethyldiaminotriphenylmethane-3'''-sulphonic acid has been obtained by oxidising the corresponding sulphinic acid, prepared by the action of sulphur dioxide and copper powder on diazotised *m'''*-aminoleuco~~malachite~~-green. When oxidised it yields a green dye similar to malachite-green. J. J. S.

Derivatives of 3-Hydroxy-1-phenyl-5-pyrazolone. MAX CONRAD and A. ZART (*Ber.*, 1906, 39, 2282—2288. Compare Michaelis and Burmeister, Abstr., 1892, 1004; 1899, i, 233).—3-Hydroxy-1-phenyl-5-pyrazolone can be prepared directly, in 64 per cent. yield from sodium, ethyl malonate, and phenylhydrazine in alcoholic solution; after removal of the alcohol, the residue is heated at 110—120° for twelve hours, cooled, dissolved in water, and, after extraction with ether, the aqueous portion is acidified and the precipitate recrystallised.

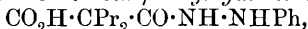
4-Amino-3-hydroxy-1-phenyl-5-pyrazolone, obtained by reducing the nitroso-compound (Michaelis, *loc. cit.*) with ammonium sulphide at 30—40°, is a yellow substance which decomposes at 320° and is insoluble in acids.

3-Hydroxy-1-phenyl-4:4-diethyl-5-pyrazolone, obtained as above from ethyl diethylmalonate, crystallises in long, prismatic needles, melts at 114—115°, and can be heated in alkaline solution for a long time without decomposition.

3-Methoxy-1-phenyl-4:4-diethyl-5-pyrazolone, obtained from an alkaline solution of the preceding compound and methyl sulphate, forms pearly leaflets, melts at 94—95°, and is soluble after long boiling in aqueous solutions of alkali hydroxides, from which sulphuric acid precipitates the unchanged substance in crystals containing 2H₂O and melting completely at 166°. Of the 2H₂O, 1 mol. is water of crystallisation, the other of constitution. Sodium hydroxide neither hydrolyses the compound nor breaks the ring (compare Michaelis (*loc. cit.*)).

3-Acetoxy-1-phenyl-4:4-diethyl-5-pyrazolone melts at 97°, and the corresponding benzoyl derivative at 110°.

3-Hydroxy-1-phenyl-4:4-dipropyl-5-pyrazolone, obtained in similar manner to the diethyl compound, forms short prisms and melts at 103—105°; dipropylmalonic acid phenylhydrazide,

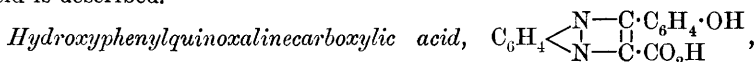


which occurs as a by-product, melts at 148° evolving carbon dioxide.

3-Hydroxy-1-phenyl-5-pyrazolonimide, $\begin{array}{c} \text{N}\cdot\text{NPh} \\ | \quad | \\ \text{OH}\cdot\text{C}\cdot\text{CH}_2 \end{array} > \text{C}\cdot\text{NH}$, obtained from sodium ethoxide, phenylhydrazine, and ethyl cyanoacetate, crystallises in prisms, melts at 219°, and is soluble in mineral acids or in alkalis. By treatment with sodium nitrite and dilute acetic acid, a quantitative yield of the isonitroso-compound is obtained, which melts and decomposes at 223°.

3-Hydroxy-1-phenyl-4:4-diethyl-5-pyrazolonimide, obtained from ethyl cyanodiethylacetate, separates from hot water in crystals containing 2H₂O, melts at 211—213°, and is not changed by boiling dilute mineral acids. C. S.

Oxidation of Naphthaphenazine by Chromic Acid. II. OTTO FISCHER and ERICH SCHINDLER (*Ber.*, 1906, 39, 2238—2244. Compare Abstr., 1904, i, 111).—A convenient method of preparing diketonaphthaphenazine by the oxidation of naphthaphenazine by chromic acid is described.



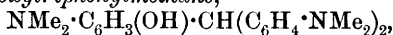
is one of the products obtained by boiling diketonaphthaphenazine with a concentrated aqueous solution of sodium hydroxide; crystallises in silvery, flat prisms or leaflets, is easily soluble in hot water, and melts at 237°, water being eliminated and the stable lactone formed. Its solution in concentrated sulphuric acid is yellow. Its barium salt forms silky needles. Its lactone, C₁₅H₈O₂N₂, formed by heating the acid either alone or with glacial acetic acid or acetic anhydride, exhibits dimorphism, separating from benzene or acetone in prisms, which are gradually transformed into hexagonal crystals; it melts at 207—208°.

The lactone may also be formed directly from diketonaphthaphenazine by oxidising it, under the conditions described, with chromic

acid. *Ketoindenephenazine*, $C_6H_4 \begin{smallmatrix} N \cdot C \\ \diagup \quad \diagdown \\ N \cdot C \end{smallmatrix} \begin{smallmatrix} \text{---} C \cdot CH \cdot CH \\ \diagdown \quad \diagup \\ C \cdot CO \cdot C \cdot CH \cdot CH \end{smallmatrix}$, formed as a by-product in the preceding reaction, separates from glacial acetic acid in yellow prisms and melts at 187° . It forms a brownish-red solution with concentrated sulphuric acid. Its *phenylhydrazone* separates from alcohol in red needles and melts at $216\text{--}217^\circ$.

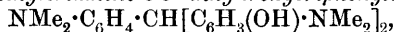
Phenylquinoxalinecarboxylic acid, $C_6H_4 \begin{smallmatrix} N \cdot C \cdot C_6H_4 \cdot CO_2H \\ \diagup \quad \diagdown \\ N \cdot CH \end{smallmatrix}$, obtained by fusing diketonaphthaphenazine with sodium hydroxide until vapours are evolved, differs from hydroxyphenylquinoxalinecarboxylic acid in being sparingly soluble in water. It melts and decomposes at about 275° , and forms a yellow solution with concentrated sulphuric acid. It is a weak acid. When distilled, it loses carbon dioxide and is transformed into phenylquinoxaline. A. McK.

***o*-Hydroxytriphenylmethane Derivatives.** EMILIO NOELTING and PAUL GERLINGER (*Ber.*, 1906, **39**, 2053—2056).—*p'p''p'''-Hexamethyl-triamino-o''-hydroxytriphenylmethane*,



obtained by condensing dimethyl-*m*-aminophenol with Michler's hydrol in an alcoholic solution of hydrogen chloride, crystallises from alcohol in colourless needles and melts and decomposes at $172\text{--}174^\circ$. It turns red in contact with the air and dissolves readily in most organic solvents, but is not readily oxidised to a dye owing to the presence of the *o*-hydroxy-group. The *acetyl* derivative, $C_{25}H_{30}ON_3Ac$, crystallises from alcohol mixed with a small amount of zinc dust in colourless needles melting at $171\text{--}173^\circ$. It changes colour more readily than the original hydroxy-compound on exposure to the air, and is readily oxidised by lead peroxide to the corresponding dye; the *additive* compound of the chloride with zinc chloride forms a dark violet powder which dyes fabrics purple-blue. The *picrate* is sparingly soluble.

p'p''p'''-Hexamethyltriamino-o''-dihydroxytriphenylmethane,



obtained by condensing dimethyl-*m*-aminophenol with dimethyl-*p*-aminobenzaldehyde in alcoholic hydrogen chloride, crystallises from dilute alcohol in colourless needles melting and decomposing at 175° . It gradually turns red on exposure to the air, and dissolves readily in organic solvents and in alkalis. The hydroxylic compound is not readily oxidised, but with acetic acid and lead peroxide yields a bluish-red dichroic solution which gives a violet-blue colour when diluted. The *diacetyl* derivative, $C_{25}H_{29}O_2N_3Ac_2$, forms a pale red mass which does not crystallise. On exposure to the air, it gradually turns blue, and can be oxidised readily to a dye, the chloride of which forms a violet powder with zinc chloride.

When the dihydroxy-derivative is warmed with concentrated sulphuric acid on the water-bath, it yields the non-crystalline *anhydro-leuco-compound*, $NMe_2 \cdot C_6H_3 \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CH(C_6H_4 \cdot NMe_2) \end{smallmatrix} C_6H_3 \cdot NMe_2$, which is readily oxidised to a dye when heated at 140° with concentrated sulphuric acid. The dye base is dark red and the salts dark green, but

produce a violet colour on the fabric. Solutions in mineral acids have an intense reddish-yellow colour and are strongly fluorescent. The compound is a dimethyl-*p*-amino-derivative of rosamine. J. J. S.

Constitution of Murexide and of Purpuric Acid. RICHARD MÖHLAU and HANS LITTER (*J. pr. Chem.*, 1906, [ii], 73, 449—472. Compare Möhlau, Abstr., 1904, i, 654; Slimmer and Stieglitz, Abstr., 1904, i, 634; Piloty and Finckh, *ibid.*, 820).—The authors consider

that the formulæ $\text{CO} \begin{array}{c} \text{NH} \text{---} \text{CO} \\ \text{NH} \cdot \text{C}(\text{OH}) \end{array} \text{C} \cdot \text{N} \cdot \text{C} \begin{array}{c} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{array} \text{CO}$ for purpuric acid and $\text{CO} \begin{array}{c} \text{NH} \text{---} \text{CO} \\ \text{NH} \cdot \text{C}(\text{O} \cdot \text{NH}_4) \end{array} \text{C} \cdot \text{N} \cdot \text{C} \begin{array}{c} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{array} \text{CO}$ for murexide are in accordance with the following facts:

The action of alloxan on ethyluramil in presence of ammonium carbonate leads to the formation of murexide and alcohol.

Alkylpurpuric acids cannot be prepared by oxidation of dibarbituryl-alkylamines. Alkylamine purpurates are formed by the action of alkylamines on alloxan and alloxantin, or of alkylamine carbonates and acetates on alloxan. The reddish-orange purpuric acid is unstable towards water. The formation of an unstable methyl purpurate by the action of methyl iodide on silver purpurate (Slimmer and Stieglitz, *loc. cit.*) is confirmed.

The relation of the constitution of murexide to its dyeing properties is discussed.

The hydrolysis of murexide by boiling water, or by cold or boiling dilute hydrochloric acid, leads to the formation on the one hand of uramil and alloxan, and on the other of alloxantin. As these products are further hydrolysed by prolonged boiling with water, their amounts are at any time a function of the duration of the hydrolysis.

Methylamine purpurate, $\text{C}_9\text{H}_{10}\text{O}_6\text{N}_6\text{H}_2\text{O}$, forms red, microscopic, rhombic crystals, or large, green, shimmering rhomboids, loses H_2O at 110° , decomposes at 210° , and when heated with water yields 7-methyluramil, alloxantin, alloxan, and methylamine.

Ethylamine purpurate, $\text{C}_{10}\text{H}_{12}\text{O}_6\text{N}_6\text{H}_2\text{O}$, forms red prisms, decomposes about 205° , and when heated with water yields alloxan, ethylamine, traces of alloxantin, and 7-ethyluramil, $\text{C}_6\text{H}_9\text{O}_3\text{N}_3$, which crystallises in hexagonal prisms.

p-Hydroxyphenylimesatine, $\text{NH} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CO} \end{array} \text{C} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, prepared by boiling isatin with *p*-aminophenol hydrochloride in alcoholic solution in presence of sodium acetate, crystallises in red prisms, melts above 300° , is insoluble in water or benzene, but is sparingly soluble in toluene, chloroform, methyl alcohol, or ethyl acetate, and is readily so in pyridine; it dissolves in aqueous alkali hydroxides forming a red, in concentrated sulphuric acid forming a reddish-brown solution, and is hydrolysed by boiling dilute acids, forming isatin and *p*-aminophenol.

p-Dimethylaminophenylimesatine, $\text{NH} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CO} \end{array} \text{C} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, prepared from isatin and dimethyl-*p*-aminoaniline, crystallises in glistening, metallic leaflets and melts at 215° .

p-Aminophenylmesatine, $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix} \text{C}:\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, crystallises in reddish-brown needles and melts above 300° . G. Y.

Action of Primary Amines on Alloxantin. RICHARD MÖHLAU and HANS LITTER (*J. pr. Chem.*, 1906, [ii], 73, 472—487. Compare Möhlau, *Abstr.*, 1904, i, 654).—Dibarbiturylalkylamines, prepared together with alloxan by boiling alloxantin, or alone by boiling dialuric acid with the hydrochlorides of primary amines in aqueous solution (Möhlau, *loc. cit.*), are colourless, crystalline, dibasic acids, dissolve in dilute alkali carbonates or hydroxides, and are hydrolysed by boiling aqueous alkali hydroxides, forming dialuric acid and the amine.

Dibarbiturylmethylamine (*loc. cit.*), which is formed also by the action of dialuric acid on 7-methyluramil, decomposes at 280° and reddens blue litmus solution. The *sodium* salt, $\text{C}_9\text{H}_7\text{O}_6\text{N}_5\text{Na}_2$, crystallises from alcohol.

Dibarbiturylethylamine, $\text{NEt}(\text{C}_4\text{H}_3\text{O}_3\text{N}_2)_2$, forms rhombic crystals, becomes red at 235° , but is not completely decomposed at 300° , and in aqueous solution has an acid reaction. The *sodium* salt, $\text{C}_{10}\text{H}_9\text{O}_6\text{N}_5\text{Na}_2$, crystallises in needles.

Dibarbiturylphenylamine, $\text{NPh}(\text{C}_4\text{H}_3\text{O}_3\text{N}_2)_2$, crystallises in white needles, becomes blue at 240° , and is oxidised superficially, becoming green on exposure to air.

Dibarbituryl- α -naphthylamine, $\text{C}_{10}\text{H}_7\text{N}(\text{C}_4\text{H}_3\text{O}_3\text{N}_2)_2$, becomes black at 260° and forms a *sodium* salt, $\text{C}_{18}\text{H}_{11}\text{O}_6\text{N}_5\text{Na}_2$, which crystallises in glistening leaflets.

Dibarbituryl- β -naphthylamine crystallises in colourless needles, decomposes at 260° , and is insoluble in indifferent solvents. The *sodium* salt, $\text{C}_{18}\text{H}_{11}\text{O}_6\text{N}_5\text{Na}_2$, crystallises in large leaflets.

The action of benzylamine on alloxantin leads to the formation of *benzyluramil*, $\text{CH}_2\text{Ph} \cdot \text{NH} \cdot \text{C}_4\text{H}_3\text{O}_3\text{N}_2$, which crystallises from hot glacial acetic acid in needles, decomposes at about 280° , and has feeble basic properties, crystallising from its solution in concentrated hydrochloric acid on cooling, but forms a *sodium* salt, $\text{C}_{11}\text{H}_9\text{O}_3\text{N}_3\text{Na}_2$; this crystallises in tetragonal prisms. When heated with aqueous sodium hydroxide, the uramil is slowly hydrolysed, forming benzylamine.

Phenylethyluramil, $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_4\text{H}_3\text{O}_3\text{N}_2$, formed by the action of β -phenylethylamine on alloxantin, crystallises in prisms, melts above 300° , is readily soluble in aqueous sodium carbonate, has feeble basic properties, and is hydrolysed by boiling sodium hydroxide, forming phenylethylamine and dialuric acid.

Dibarbiturylcarbamide, $\text{CO}(\text{NH} \cdot \text{C}_4\text{H}_3\text{O}_3\text{N}_2)_2$, is formed by boiling alloxantin with carbamide and hydrochloric acid in aqueous solution in a reflux apparatus; it crystallises in spears, decomposes above 300° , and is readily soluble in aqueous sodium carbonate or alkali hydroxides, forming solutions which evolve ammonia when boiled.

Alloxazine (Kühling, *Abstr.*, 1891, 1341), prepared from alloxantin and *o*-phenylenediamine hydrochloride, forms a greyish-green powder and decomposes above 300° . The *sodium* salt, $\text{C}_{10}\text{H}_4\text{O}_2\text{N}_4\text{Na}_2$, crystallises in yellow needles.

Alloxantin and *m*-phenylenediamine hydrochloride interact, forming a dark brown to black, amorphous *precipitate*.

Bisanhydroalloxan-p-phenylenediamine, $C_6H_4(N \cdot C_4H_3O_3N_2)_2$, prepared from alloxantin and *p*-phenylenediamine hydrochloride, forms blue needles with green lustre, melts above 300° , and dissolves in concentrated sulphuric acid or aqueous alkali hydroxides or carbonates, forming a bluish-violet solution. When boiled with an aqueous alkali hydroxide, it is hydrolysed to the diamine and alloxan, the solution becoming colourless, but as the solution cools the anhydro-compound is re-formed.

Dibarbituryl-p-phenylenediamine, $C_{14}H_{12}O_6N_6$, is formed by the action of dialuric acid on *p*-phenylenediamine hydrochloride; it crystallises in colourless prisms, is readily soluble in aqueous sodium carbonate or hydroxide, and when boiled with alloxan in aqueous solution is oxidised slowly, in ammoniacal solution more rapidly, yielding bisanhydro-alloxan-*p*-phenylenediamine.

Dibarbituryl-2:5-tolylenediamine, $C_6H_3Me(NH \cdot C_4H_3O_3N_2)_2$, prepared from alloxantin and tolylene-2:5-diamine hydrochloride, forms colourless crystals, melts above 300° , is readily soluble in aqueous sodium hydroxide or carbonate or concentrated hydrochloric acid, and when oxidised with potassium permanganate in hot dilute sulphuric acid solution yields a blue, flocculent *product* (*bisanhydroalloxan-2:5-tolylenediamine*?).

Dibarbiturylbenzidine, $C_{12}H_8(NH \cdot C_4H_3O_3N_2)_2$, prepared from alloxantin and benzidine hydrochloride, is obtained as a greyish-white, amorphous, flocculent substance, and is not hydrolysed by boiling aqueous sodium hydroxide; the *sodium* salt, $C_{20}H_{14}O_6N_6Na_2$, crystallises in colourless needles. G. Y.

Mixed Azo-compounds. II. ALEXANDER EIBNER and O. LAUE (*Ber.*, 1906, **39**, 2022—2027).—1-Phenyl-3-methylpyrazoloneazobenzene (*Abstr.*, 1903, i, 871) reacts with a chloroform solution of bromine, yielding dark reddish-brown crystals of the perbromide, $C_{16}H_{12}ON_4Br_6$, which with ammonia yields *dibromophenylmethylpyrazoloneazobenzene*, $C_{16}H_{12}ON_4Br_2$. This crystallises from a mixture of ether and chloroform in slender, orange-red needles and melts at 227° .

With sodium hydroxide or, better, sodium ethoxide, it yields a crystalline *sodium* derivative, $C_{16}H_{11}ON_4Br_2Na$, and when reduced with tin and hydrochloric acid it yields dibromorubazonic acid, melting at above 300° , and *p*-bromoaniline. It has not been found possible to couple mono-substituted pyrazolone derivatives which contain the substituent in the methylene group with diazobenzene.

Phenylhydrazineketopyrazolonecarboxylic acid does not yield a perbromide, but simply a mono-substituted derivative, $C_{10}H_{11}O_3N_4Br$, which crystallises from glacial acetic acid in golden-yellow needles and melts at 258° .

Phenylhydrazineketopyrazolone dissolves in sodium hydroxide solution, and with a chloroform solution of bromine yields a *perbromide*, $C_{15}H_{11}ON_4Br_3$. This crystallises in dark reddish-brown prisms and reacts with alkali, yielding compact crystals of a *bromo*-derivative,

$C_{15}H_{11}ON_4Br$, melting at 224° . When reduced with zinc dust and acetic acid, the carboxylic acid yields aniline and rubazonecarboxylic acid (Bernthsen, *Chem. Zeit.*, 1898, 457). The monobromo-derivative yields *p*-bromoaniline and rubazonecarboxylic acid.

These reactions indicate that the acid is an azo-compound, namely, the carboxylic acid of ketophenylpyrazoloneazobenzene. The views of Bernthsen and R. Meyer regarding the structure of tartrazin are thus confirmed.

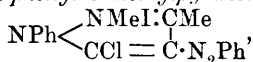
Ketophenylpyrazoloneazocarboxylic acid yields a *disodium* derivative, $C_{16}H_{10}O_3N_4Na_2$, in the form of golden-yellow crystals which are readily hydrolysed by water to the monosodium salt. *cyclo*Pentadieneazobenzene also forms a *perbromide*. J. J. S.

Benzeneazo-derivatives of Antipyrine and Thiopyrine. AUGUST MICHAELIS and H. SCHLECHT (*Ber.*, 1906, 39, 1954—1956).—

4-Benzeneazoantipyrine, $NPh \begin{matrix} \swarrow NMe: CMe \\ >O \\ \searrow C=C \cdot N_2Ph \end{matrix}$, is formed by heating

4-benzeneazo-1-phenyl-3-methyl-5-pyrazolone with methyl sulphate; it crystallises in reddish-yellow leaflets, melts at 174° , is readily soluble in alcohol or in hydrochloric acid, forming a deep red solution, and is insoluble in aqueous sodium hydroxide.

4-Benzeneazo-5-chloro-1-phenyl-3-methylpyrazole methiodide,



is prepared by treating 4-benzeneazo-5-chloro-1-phenyl-3-methylpyrazole (Michaelis and Leonhardt, *Abstr.*, 1904, i, 124) with an excess of methyl sulphate, neutralising the product with sodium carbonate, and adding a concentrated solution of potassium iodide; it crystallises in slender, yellow needles and melts at 170° . The *methochloride*, prepared by boiling the methiodide with silver chloride in aqueous-alcoholic solution, forms reddish-yellow crystals and melts at 164° .

When treated with potassium hydrogen sulphide in aqueous solution,

the methiodide yields 4-benzeneazothiopyrine, $NPh \begin{matrix} \swarrow NMe: CMe \\ >S \\ \searrow C=C \cdot N_2Ph \end{matrix}$,

which forms stout, dark red crystals, melts at 216° , is readily soluble in alcohol, and with acids forms unstable, dark red salts (compare Michaelis, Leonhardt, and Wahle, *Abstr.*, 1905, i, 392). G. Y.

The Rendering Insoluble of Gelatin during Photographic Development, particularly by the Use of Pyrogallol Developers. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1906, [iii], 35, 377—381. Compare *Abstr.*, 1905, i, 847, 848).—The results of experiments with a number of developers show that gelatin only becomes insoluble when the developers are in presence of alkali and in contact with air, and that probably the active agents in rendering the gelatin insoluble are the oxidation products formed from the developers. Where the oxidation product is insoluble in dilute alkalis, as in the case of *p*-aminophenol, the action is slight. The action is usually most marked

in the neighbourhood of the reduced silver, and this is probably due to the more rapid oxidation of the developer in that region by the bromine liberated.

T. A. H.

Action of Ozone and other Oxidising Agents on Lipase. JOSEPH H. KASTLE (*Chem. Centr.*, 1906, i, 1555—1556; from *Public Health and Marine-Hospital Service of the U.S. Hygienic Lab. Bull.* No. 26, 37—41).—The activity of a quantity of lipase from pig's liver which was found capable of hydrolysing 0.058 gram of ethyl butyrate in four and a quarter hours was destroyed by the action of 1.009 mg. of ozone in forty minutes. When a second quantity of lipase, which under normal conditions hydrolysed 0.058 gram of ethyl butyrate in twenty-four hours, was treated with 0.312 mg. of ozone, its hydrolytic action sank to 0.00116 gram in twenty-four hours.

Silver nitrate, hydriodic acid, formaldehyde, cresols, hydrocyanic acid, potassium nitrate, and succinic acid had practically no poisonous action on lipase; mercuric chloride, chromic acid, copper sulphate, and perosmic acid were moderately poisonous; ozone, chlorine, bromine, sodium fluoride, cyanogen iodide, and potassium permanganate were strongly poisonous. The poisonous effect of cyanogen iodide increased with rise of temperature.

E. W. W.

Stability of Oxydases and their Behaviour towards Various Reagents. JOSEPH H. KASTLE (*Chem. Centr.*, 1906, i, 1554—1555; from *Public Health and Marine-Hospital Service of the U.S. Hygienic Lab. Bull.* No. 26, 7—22).—The oxydase of *Sepiota americana* retains its activity for weeks or months and appears to be more stable in glycerol than in water. The presence of oxydases has been detected in the aqueous and glycerol extracts of a number of moulds indigenous to Columbia, but not in the extracts of the very poisonous *Amanita verna*. Whilst the oxidising action of the glycerol extracts of *Lactarius piperatus*, *Lactarius volumen*, and *Lactarius indigo* did not decrease in four months, in other cases, for instance, in that of *Volvaria bombycina*, the activity of the extract rapidly diminished. The oxydases are less stable in water than in glycerol and are not so rapidly destroyed by toluene as by chloroform or thymol. The oxydases of *Lepiota americana* are precipitated from the aqueous solution by alcohol in a colloidal form. An aqueous solution of material which had been dried in the air and exposed for four and a half months gave a strong blue coloration with guaiacum tincture. The oxidising power of the substance is destroyed at 80—90°, but it withstands heating for a short time at 80°. When the fresh mould is kept for some time in an atmosphere of hydrogen, reducing substances are formed which decolorise guaiacum-blue; the formation of these compounds may be due to anaërobic bacteria or to the mould itself. The oxydase is more readily soluble in water than in other solvents, and is not destroyed by a 40 per cent. solution of formaldehyde; it is insoluble in ethyl or amyl alcohol and its activity is not affected. It dissolves in glycerol and apparently to a certain extent in toluene. Certain substances such as chlorine hydrate completely destroy the oxydase.

A deep purple-red coloration is produced when aqueous potato

extract is added to a slightly alkaline solution of leucorosolic acid, but strongly alkaline or acid solutions are scarcely oxidised. The ethyl ester of phenolphthalein gives a similar reaction, but the presence of bromine in the ethyl ester of tetrabromophenolphthalein appears to prevent oxidation by vegetable oxydases; benzoyl peroxide and benzoyl acetyl peroxide oxidise the latter compound, however, forming a bluish-green coloration. An alcoholic solution of aloin gives a red coloration with vegetable oxydases; the sensitiveness of the reagent is considerably increased by shaking with zinc dust, filtering, and exposing to air for a short time, but it loses its property in some days. The red substance which is formed is soluble in water and in the aqueous extracts containing oxydases; it is more stable than the blue compound formed by the oxidation of guaiacum tincture. The sensitiveness of the aloin and guaiacum reactions is about the same. The intensity of the peroxydase reaction of aloin in aqueous extracts of the leaves of *Phytolacca decandra* depends on the concentration of the hydrogen peroxide, but if only small quantities are used there is but little variation. Whilst the peroxydase reaction of extracts of horseradish, potato parings, and other vegetable oxydases is improved by the addition of a small quantity of hydrogen peroxide, larger quantities are required in the case of animal oxydases. E. W. W.

Peroxydases as Specifically-acting Enzymes. ALEXIS BACH (*Ber.*, 1906, 39, 2126—2129).—Tyrosine is not oxidised by the system peroxydase—hydrogen peroxide, although the oxidation reactions of ordinary oxydases are effected by this system. The specific action of tyrosinase in oxidising tyrosine is to be ascribed either to the specific nature of its peroxydases or of its oxygenases (since all oxydases are mixtures of peroxydases and oxygenases); the author has accordingly separated, with partial success, the peroxydases of tyrosinase from the oxygenases. Potato juice was used; the fresh juice oxidised tyrosine rapidly, whilst after the treatment with alcohol described, the oxygenases were almost entirely destroyed; the final product contained peroxydases, but had very little oxidising action on tyrosine. On the supposition that the falling off of the tyrosine action was due to the partial destruction of the oxygenases, the latter were replaced by hydrogen peroxide, the addition of which caused the solution to exert an oxidising action on tyrosine.

Similar results were obtained with the mixture of ordinary oxydases and of tyrosinase contained in the juice of *Lactarius velereus*. The specific action of tyrosinase is due to the specific nature of its peroxydases.

Various theoretical considerations are adduced.

A. McK.

Organic Chemistry.

Purification of Acetylene by means of Calcium Hypochlorite. HUGO DITZ (D.R.-P. 162324).—In the purification of acetylene by means of commercial bleaching powder, spontaneous heating occurs, and explosions may arise from the formation of chlorine and nitrogen chloride. This is avoided by using the definite compound $\text{CaO}, \text{CaOCl}_2, 2\text{H}_2\text{O}$ or the compound $\text{CaO}, \text{CaOCl}_2, \text{H}_2\text{O}$, obtained by heating the former (Abstr., 1901, ii, 239). These substances do not evolve chlorine when heated, but decompose at $130\text{--}140^\circ$, evolving oxygen. C. H. D.

aci-Esters of Nitroform. ARTHUR HANTZSCH and K. S. CALDWELL (Ber., 1906, 39, 2472—2478).—*aci*-Methylnitroform has not been obtained, but in the reaction between methyl iodide and silver nitroform a small amount of nitroform is always obtained, the quantity increasing with diminishing temperature; its production is due to the hydrolysis of the *aci*-methyl ester by the water from the hydrated silver nitroform.

Ethereal solutions of hydrated silver nitroform and of methyl iodide react at -75° with the instantaneous separation of an intensely yellow substance, *aci-silver nitroform di-methyl iodide*, $\text{C}(\text{NO}_2)_2:\text{NO}\cdot\text{OAg}, 2\text{MeI}$, which from the rapidity of its formation is regarded as an additive compound and not as having the constitution $\text{C}(\text{NO}_2)_2:\text{NO}\cdot\text{OMe}, \text{AgI}, \text{MeI}$. The substance is very unstable and decomposes spontaneously at $6\text{--}8^\circ$ in air or in indifferent anhydrous solvents into silver iodide and trinitroethane, but in the presence of water nitroform is produced quantitatively.

The theoretical importance of these decompositions is discussed.

Benzyl iodide and allyl iodide yield similar additive compounds which are even less stable. Ethyl iodide, which at the ordinary temperature yields trinitropropane, an oil with the odour of nitrous acid, does not react at low temperatures with silver nitroform.

C. S.

Trinitromethane and Triphenylmethane. ARTHUR HANTZSCH (Ber., 1906, 39, 2478—2486).—[With K. S. CALDWELL.]—*Iodopiecin*, $\text{CI}(\text{NO}_2)_3$, obtained from iodine and silver nitroform, melts and turns brown at 58° , is decomposed by silver nitrate, slowly in the cold, more rapidly on boiling, reacts with potassium hydroxide in accordance with the equation $3\text{CI}(\text{NO}_2)_3 + 6\text{KOH} = 3\text{C}(\text{NO}_2)_3\text{K} + 2\text{KI} + \text{KIO}_3 + 3\text{H}_2\text{O}$, and with silver nitrite yields tetranitromethane. Hexanitroethane is not obtained in the preceding preparation, or by treatment of iodopiecin with silver nitroform, and the author uses this fact as an argument for regarding Gomberg's triphenylmethyl as hexaphenylethane.

The paper is mainly polemical.

C. S.

Aliphatic Polynitro-compounds. JAKOB MEISENHEIMER and M. SCHWARZ (*Ber.*, 1906, 39, 2543—2552).—Trinitroethane and potassium ethoxide react to form the potassium derivative of a substance which was regarded by Hantzsch and Rinckenberger (*Abstr.*, 1899, i, 404) as ethyl *aci*-dinitroethane, $\text{O}\cdot\text{N}(\text{OEt})(\text{OK})\cdot\text{CHMe}\cdot\text{NO}_2$, and by Meisenheimer (*Abstr.*, 1903, i, 223) as dinitrodiethyl ether, $\text{OEt}\cdot\text{CH}_2\cdot\text{C}(\text{NO}_2)\cdot\text{NO}\cdot\text{OK}$.

That the latter view is correct is proved by the following considerations. The substance, after crystallisation from alcohol, has the composition $\text{C}_4\text{H}_7\text{O}_6\text{N}_2\text{K}$, forms a bromine derivative, $\text{C}_4\text{H}_7\text{O}_6\text{N}_2\text{Br}$, which is a colourless oil boiling at $103\text{--}104^\circ$ under 13 mm. pressure, and by acidification yields dinitrodiethyl ether, $\text{C}_4\text{H}_8\text{O}_5\text{N}_2$, a heavy, colourless oil which boils at 100° under 11 mm. pressure.

The potassium derivative of the corresponding methyl dinitroethyl ether, $\text{OMe}\cdot\text{CH}_2\cdot\text{C}(\text{NO}_2)\cdot\text{NO}\cdot\text{OK}$, is reduced by tin and hydrochloric acid to methoxyacetic acid, $\text{OMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. A reaction similar to the one in question takes place between trinitroethane and potassium cyanide in methyl-alcoholic solution, whereby the potassium salt of *aci*-dinitropropionitrile, $\text{CN}\cdot\text{CH}_2\cdot\text{C}(\text{NO}_2)\cdot\text{NO}\cdot\text{OK}$, is obtained; it separates from water in glistening, yellow leaflets, and by treatment with aqueous silver nitrate yields the explosive silver salt, $\text{C}_3\text{H}_2\text{O}_4\text{N}_3\text{Ag}$, which forms yellow needles. The nitrile, $\text{CN}\cdot\text{CH}_2\cdot\text{CH}(\text{NO}_2)_2$, obtained by acidifying the potassium derivative, is an oil which cannot be distilled without decomposition, but by keeping in a vacuum over sulphuric acid it solidifies to a mass of deliquescent, yellow needles.

Methyl $\beta\beta$ -dinitropropionate, $\text{CH}(\text{NO}_2)_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$, is obtained by treating potassium dinitropropionitrile, suspended in methyl alcohol, with hydrogen chloride; the crude ester is dissolved in methyl alcohol, cooled, and slowly treated with 10 per cent. methyl-alcoholic potash, and the potassium derivative, $\text{C}_4\text{H}_5\text{O}_6\text{N}_2\text{K}$, which separates as an amorphous precipitate, is crystallised from water and methyl alcohol and acidified, when the pure methyl ester is obtained as a colourless oil. Dinitropropionitrile is hydrolysed by concentrated hydrochloric acid, forming dinitropropionic acid, a viscous, green oil, which explodes when heated; the potassium salt is precipitated from alcoholic solution as a yellow, flocculent precipitate.

By treatment with 10 per cent. hydrogen peroxide, potassium dinitropropionitrile yields cyanoacetic acid, which was identified by its conversion into malonic acid. When a methyl-alcoholic solution of trinitroethane is treated with an alkaline solution of hydroxylamine, a quantitative yield of potassium *aci*-dinitroethane is obtained. Iodo-trinitromethane, $\text{CI}(\text{NO}_2)_3$, obtained from iodine and silver nitroform in ethereal solution, forms yellow leaflets, melts at $55\text{--}56^\circ$, distils and slightly decomposes at $48\text{--}48\cdot5^\circ$ under 13 mm. pressure, and undergoes decomposition when quickly heated (compare preceding abstract).
C. S.

Some Synthetical Reactions of Pinacolin. LOUIS HENRY (*Compt. rend.*, 1906, 143, 20—22).—Pinacolin reacts with magnesium methyl bromide to form pentamethylethanol in the form of its crystalline hydrate, $\text{CMe}_3\cdot\text{CMe}_2\cdot\text{OH}\cdot\text{H}_2\text{O}$ (compare Butleroff, this Journal,

1875, 1248), which can also be prepared from acetone by the action of magnesium *ter*-butyl chloride. Pinacolin combines with anhydrous hydrogen cyanide, or with a 25 per cent. solution of the acid, to form β -cyano- $\gamma\gamma$ -dimethylbutan- β -ol, $\text{CMe}_3\cdot\text{CMe}(\text{OH})\cdot\text{CN}$ (compare Carlinfanti, Abstr., 1898, i, 234; 1899, i, 671), which crystallises in white needles, melts at 94° (Carlinfanti found 82 – 87°), is insoluble in water, and very soluble in ether, alcohol, light petroleum, or glacial acetic acid; the *acetyl* derivative, $\text{CMe}_3\cdot\text{CMe}(\text{OAc})\cdot\text{CN}$, is a pale yellow, slightly viscous liquid, possessing a peculiar sour-sweet odour; it boils at 228 – 230° under 770 mm. pressure, has a sp. gr. 0.9535 at 20° , and n_D 1.43091. M. A. W.

Preparation of Pinacone. ARNOLD F. HOLLEMAN (*Rec. trav. chim.*, 1906, 25, 206–207).—A modification of Couturier and Meunier's method for the preparation of pinacone (Abstr., 1905, i, 326). When a solution of 20 grams of mercuric chloride in 200 grams of dry acetone is allowed to drop slowly on to 20 grams of bright magnesium wire in a reflux apparatus, a violent action occurs and the acetone boils; the reaction is completed by heating the contents of the flask until all the acetone has disappeared; this requires from one to two hours; water is then added and the pinacone separated from the mixture by distillation; the yield is 70 grams. M. A. W.

Preparation of the Chlorohydrin, the Oxide, and an Unsaturated Alcohol from Normal Diprimary Decylene Glycol [Decan-*ak*-diol]. LEO ALBERTI and BRONISLAV SMIECIUSZEWSKI (*Monatsh.*, 1906, 27, 411–419. Compare Scheuble, Abstr., 1904, i, 3).—The *chlorohydrin*, $\text{CH}_2\text{Cl}\cdot[\text{CH}_2]_8\cdot\text{CH}_2\cdot\text{OH}$, prepared by heating decylene glycol with hydrochloric acid of sp. gr. 1.19 in a reflux apparatus on the water-bath, is obtained as a strongly refracting, colourless oil which boils at 164 – 165° under 20 mm. pressure, and is readily soluble in ether, alcohol, benzene, or light petroleum. When heated with powdered, freshly fused sodium hydroxide, the chlorohydrin yields a mixture of the corresponding oxide and an unsaturated alcohol.

Decamethylene oxide, $\text{C}_{10}\text{H}_{20}\text{O}$, is obtained as a transparent liquid which boils at 181° , does not form an additive compound with bromine, and is not acted on by zinc ethyl at 180° , or by water at 200° , but yields the chlorohydrin when heated with concentrated hydrochloric acid at 110° .

The *unsaturated alcohol*, $\text{C}_{10}\text{H}_{20}\text{O}$, boils at 234 – 238° , and when heated with acetic anhydride and sodium acetate at 130° forms an *acetate*, $\text{C}_{12}\text{H}_{22}\text{O}_2$, which boils at 242 – 246° and forms an additive compound with 1 mol. of bromine. G. Y.

$\alpha\beta$ -Trichloroethyl Ether. II. GIUSEPPE ODDO and EFISIO MAMELI (*Gazzetta*, 1906, 36, i, 480–490. Compare Abstr., 1904, i, 280).—The action on $\alpha\beta$ -trichloroethyl ether of an aqueous solution of potassium hydroxide or ethylamine or sodium hydrogen sulphite yields the same products as, but proceeds more rapidly than, the action of water.

The first phases of the action of dry ammonia on $\alpha\beta$ -trichloroethyl ether proceed according to the equations: (1) $\text{CHCl}_2 \cdot \text{CHCl} \cdot \text{OEt} + 2\text{NH}_3 = \text{CHCl}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{OEt} + \text{NH}_4\text{Cl}$; (2) $2\text{CHCl}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{OEt} = \text{CHCl}_2 \cdot \text{CH}(\text{OEt})_2 + \text{CHCl}_2 \cdot \text{CH}(\text{NH}_2)_2$. The last compound is, however, unstable, and gives rise to resinous, complex nitrogen compounds of basic character.

Powdered magnesium has little action on $\alpha\beta$ -trichloroethyl ether, either by itself or in presence of a solvent. When benzene is used as solvent and the mixture is heated in a reflux apparatus, aldehydic vapours are evolved and dichloroacetal and a small quantity of a product of low boiling point are formed.

Zinc dust acts readily on $\alpha\beta$ -trichloroethyl ether with formation of dichloroaldehyde and large quantities of hydrogen chloride, but no organo-zinc compound of the formula $\text{CHCl}_2 \cdot \text{CH}(\text{OEt}) \cdot \text{ZnCl}$ could be obtained.

Reduction of the trichloro-ether by powdered zinc or magnesium and a stream of dry hydrogen chloride, or by zinc and acetic acid, gives mainly dichloroaldehyde, together with a fraction boiling at $80-90^\circ$ under 10 mm. pressure, which is probably $\beta\beta$ -dichloroethyl ether.

Dichloromonothioacetal, $\text{SEt} \cdot \text{CH}(\text{OEt}) \cdot \text{CHCl}_2$, prepared by the interaction of $\alpha\beta$ -trichloroethyl ether (1 mol) and ethyl mercaptan (1 mol.), boils at $110-125^\circ$ under 20–30 mm. pressure.

Phenylethyl dichloroacetal, $\text{OEt} \cdot \text{CH}(\text{OPh}) \cdot \text{CHCl}_2$, obtained by the action of sodium phenoxide on $\alpha\beta$ -trichloroethyl ether, boils at $165-170^\circ$ under 40 mm. pressure, reacts energetically with nitric acid, combines with bromine giving a white compound, decolorises permanganate, dissolves in alcohol, and readily decomposes even in a closed vessel in the dark.

$\alpha\beta$ -Trichloroethyl ether (1 mol.) combines with pyridine (1 mol.), forming a substance which, with platinum chloride, gives a compound, $(\text{CHCl}_2 \cdot \text{CHCl} \cdot \text{OEt}, \text{C}_5\text{NH}_5)_2, \text{PtCl}_4$, crystallising from dilute hydrochloric acid in orange-yellow needles, melting and decomposing at $208-209^\circ$, and, with gold chloride, a yellow compound,

$(\text{CHCl}_2 \cdot \text{CHCl} \cdot \text{OEt}, \text{C}_5\text{NH}_5)_2, \text{AuCl}_3$,
melting at $92-93^\circ$.

T. H. P.

Course of the Decomposition of Mixed Aliphatic Ethers by Hydrogen Iodide. ARTHUR MICHAEL and FRANCIS D. WILSON (*Ber.*, 1906, 39, 2569–2577. Compare da Silva, this Journal, 1876, i, 60; Lippert, *Abstr.*, 1893, i, 620).—When methyl propyl ether is treated with hydrogen iodide at 0° , an additive compound, $\text{C}_4\text{H}_{10}\text{O}, \text{HI}$, is formed, which is subsequently decomposed. The products are well washed with water, dried with phosphoric oxide, and fractionated, whereby mainly methyl iodide is obtained, the very small quantity of propyl iodide formed being identified in the form of silver propionate.

Ethyl propyl ether yields a similar additive compound, $\text{C}_5\text{H}_{12}\text{O}, \text{HI}$, which is decomposed at 100° ; from the products, after treatment as above, ethyl and propyl iodides were isolated. The additive compound, $\text{C}_6\text{H}_{14}\text{O}, \text{HI}$, obtained from propyl isopropyl ether, is decomposed at 100° , and the products treated as before.

The mixed propyl and isopropyl iodides are converted into the aldehyde and ketone respectively, and identified in the form of the hydrazones.

From considerations of the heats of formation of the alkyl iodides, and also of the energy required to separate the different alkyl groups from oxygen, the authors conclude that an ether containing methyl and a primary or secondary alkyl group will yield methyl iodide and alkylcarbinol by treatment with hydrogen iodide, whilst methyl alcohol and a tertiary alkyl iodide will result from an ether containing the methyl and a tertiary alkyl group. Moreover, an ether containing two primary, two secondary, or two such mixed alkyl groups will yield a mixture of haloids and alcohols containing each of the alkyl groups. C. S.

Electrolytic Preparation of Alkyloxides and Alkyl-carbonates. BÉLA SZILÁRD (*Zeit. Elektrochem.*, 1906, 12, 393—395).—When a solution of sodium ethoxide (4 per cent.) in pure anhydrous alcohol is electrolysed with platinum electrodes and a current density just sufficient to produce a small evolution of gas at the anode, sodium ethyl carbonate is formed as a solid deposit at the anode. The yield is about one-seventh of the theoretical quantity. Sodium methyl carbonate is formed in a similar way. Using a magnesium anode, magnesium ethyl (or methyl) carbonate is obtained. Using a lead anode, a one per cent. sodium methoxide solution, and a small current density, lead methoxide, $\text{Pb}(\text{OMe})_2$ is formed; with higher current densities, salts containing increasing quantities of carbon dioxide are produced. Copper methoxide, $\text{Cu}(\text{OMe})_2$, was obtained in a similar way. T. E.

Preparation of the Anhydrides of Monobasic Organic Acids. VEREIN FÜR CHEMISCHE INDUSTRIE IN FRANKFURT (D.R.-P. 167304).—When a mixture of chlorine and sulphur dioxide containing a slight excess of the latter gas is passed into a cooled intimate mixture of anhydrous sodium and calcium acetates, acetic anhydride is produced and obtained by distilling the mixture, preferably under reduced pressure (compare Abstr., 1906, i, 3). G. T. M.

Reactions of Double Decomposition between Alcohols and Esters. GIUSEPPE BRUNI and ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 637—644).—The authors have heated mixtures, in molecular proportions, of menthol with ethyl acetate, ethyl benzoate, ethyl oxalate, or ethyl malonate, in order to determine whether any double decomposition takes place under these conditions, the changes being followed by means of the rotatory power. With ethyl acetate, no change occurs after heating for ten hours at 100° , and the same is the case with ethyl benzoate after twelve hours' heating at 80° . With ethyl oxalate and ethyl malonate, however, double decomposition proceeds at an appreciable velocity when they are heated at 100° with menthol.

With ethyl acetoacetate (2 mols.) and menthol (1 mol.), or with

menthyl acetoacetate (1 mol.), ethyl alcohol (1 mol.), and ethyl acetoacetate (1 mol.), double decomposition takes place, equilibrium being reached after heating at 100° for twenty-four hours, when 57·6 per cent. of the menthol has been transformed into menthol acetoacetate. At 79·9°, however, equilibrium is not attained, even after 155 hours, although the final condition of equilibrium is the same at this temperature as at 100°. The values of K , calculated according to the equation for a bimolecular reaction, are not constant, but decrease as the time increases. T. H. P.

Preparation of Solid Fatty Acids. CARL DREYMAN (D.R.-P. 166610).—The ordinary process for obtaining solid fatty acids from the unsaturated fatty acids or their glycerides depends on the treatment of these substances with strong sulphuric acid at 60—120°, the subsequent washing out of this acid with water or brine solution, and the distillation of the product. The final operation is attended by a certain amount of destructive action due to the decomposition of the hydroxystearic acid which is present. This effect is due to the presence of sulphuric acid, which is tenaciously retained by the organic matter in spite of the washing with water. The distillation may, however, be greatly improved by the introduction of some oxide, carbonate, or other acid-fixing substance, which neutralises the mineral acid, and thus prevents the formation of hydrocarbons and tar.

G. T. M.

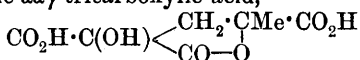
Measurements of Affinity of Monobasic Unsaturated Fatty Acids. FRITZ FICHTER and HERMANN MUELLER (*Annalen*, 1906, 348, 256—259. Compare Fichter and Pfister, *Abstr.*, 1904, i, 965).—The affinity constants of a number of monobasic $\alpha\beta$ - and $\beta\gamma$ -unsaturated fatty acids have been measured by means of the inversion of sucrose and of the hydrolysis of methyl acetate; the results, which are given in the following table, confirm Fichter and Pfister's observation that the $\beta\gamma$ -unsaturated acids have the larger affinity constants:

	Inversion of sucrose. $K \times 10^{-4}$.	Hydrolysis of methyl acetate. $K \times 10^{-4}$.
Butyric acid.....	0·0569	0·0206
Crotonic acid	0·0723	0·0320
Vinylacetic acid	0·0941	0·0540
<i>n</i> -Valeric acid	0·0545	0·0164
$\alpha\beta$ -Pentenoic acid	0·0691	0·0170
$\beta\gamma$ -Pentenoic acid	0·1738	0·0668
α -Methyl- $\alpha\beta$ -pentenoic acid ..	0·0284	0·0235
α -Methyl- $\beta\gamma$ -pentenoic acid...	0·0757	0·0325

α -Ethyl- $\alpha\beta$ -pentenoic acid has the dissociation constant $K = 0·00205$, and α -ethyl- $\beta\gamma$ -pentenoic acid, $K = 0·00339$.

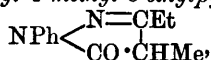
The heat of combustion of α -methyl- $\alpha\beta$ -pentenoic acid is 795·7 Cal., whilst that of α -methyl- $\beta\gamma$ -pentenoic acid is 797·9 Cal. (compare Thiele, *Abstr.*, 1899, i, 554). G. Y.

Transformations of Salts of Pyruvic Acid. IV. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1906, 25, 229—232. Compare Abstr., 1902, i, 72; 1903, i, 146; 1904, i, 550).—Barium parapyruvate, $C_6H_6O_6Ba, 4H_2O$, prepared by the condensation of barium pyruvate spontaneously or by means of baryta, loses $3H_2O$ when exposed over sulphuric acid. The impurity present in small quantity in barium parapyruvate which has been prepared by the action of potassium cyanide on barium pyruvate is sparingly soluble in boiling water, and dissolves in hydrochloric acid; the solution on evaporation over sulphuric acid and quicklime deposits crystals of a compound which has the empirical formula $C_7H_8O_7, \frac{1}{2}H_2O$, and is probably the α -lactone of α -dihydroxybutane- α -tricarboxylic acid,

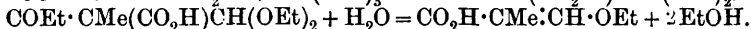
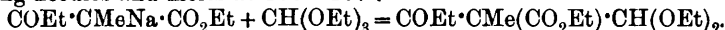


The hydrated compound softens at 100° and decomposes at 180° , the anhydrous compound decomposes at 195° . M. A. W.

Derivatives of Ethyl Propionylpropionate. OSKAR EMMERLING and L. KRISTELLER (*Ber.*, 1906, 39, 2450—2455).—When ethyl propionylpropionate is heated with phenylhydrazine on the water-bath and finally at 140° , 1-phenyl-4-methyl-3-ethylpyrazolone,



is obtained; it melts at 112.5° and yields the corresponding salt with hot dilute hydrochloric or sulphuric acid. When heated with methyl iodide and methyl alcohol at 110° , it forms 1-phenyl-2:4-dimethyl-3-ethylpyrazolone, $C_{13}H_{16}ON_2$, which melts at 37.5° , boils at $208-210^\circ$ under 18 mm. pressure, and forms a *platinichloride*, $2C_{13}H_{16}ON_2, H_2PtCl_6, 2H_2O$. The interaction of chloroform and the reaction product of sodium and ethyl propionate leads to the formation of β -ethoxymethylacrylic acid, $OEt \cdot CH : CMe \cdot CO_2H$, which separates from light petroleum in leaflets or long needles and melts at $106-107^\circ$.



The *potassium*, *barium*, *calcium*, *silver*, and *cadmium* salts are mentioned; the *ethyl* ester boils at $198-199^\circ$ and has an aromatic odour.

The acid is stable towards cold dilute mineral acids, but by warming yields carbon dioxide, alcohol, and propaldehyde; it absorbs bromine to form a yellow, crystalline additive compound, $C_6H_{10}O_8Br_2$.

The constitution of the acid has been verified by its production from β -bromomethylacrylic acid, sodium ethoxide, and alcohol at $130-140^\circ$.

Hantzsch and Wohlbrück's acid, $C_6H_8O_3$ (Abstr., 1887, i, 717), obtained by warming ethyl bromopropionylpropionate, melts, not at $106-108^\circ$, but at 124° , and does not yield β -methoxymethylacrylic acid when reduced. C. S.

Crystallographic Description of Alkali Cobaltioxalates.

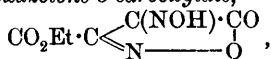
H. COPAUX (*Chem. Centr.*, 1906, i, 1604; from *Bull. Soc. franç. Min.*, 29, 67—76. Compare Abstr., 1902, i, 586).— $(NH_4)_6Co_2(C_2O_4)_6, 6H_2O$

is monoclinic and isomorphous with the ammonium oxalates of aluminium, chromium, and iron [$a:b:c=1.0017:1.03929$; $\beta=92^{\circ}44'$]. $K_6Co_2(C_2O_4)_6 \cdot 7H_2O$, triclinic [$a:b:c=0.5963:1.06590$; $\alpha=88^{\circ}22'$, $\beta=91^{\circ}42'$, $\gamma=101^{\circ}23'$]. $Rb_6Co_2(C_2O_4)_6 \cdot 8H_2O$, rhombic [$a:b:c=1.1485:1.25960$]. $Na_6Co_2(C_2O_4)_6 \cdot 10H_2O$ is monoclinic and isomorphous with the corresponding oxalates of aluminium, chromium, and iron [$a:b:c=1.398:1.1293$]. $Li_6Co_2(C_2O_4)_6 \cdot 12H_2O$ is triclinic and is isomorphous with the lithium oxalates of aluminium and chromium [$a:b:c=1.0177:1.07885$; $\alpha=94^{\circ}22'$, $\beta=81^{\circ}$, $\gamma=109^{\circ}4'$]. $K_5Na_{10}Co_8(C_2O_4)_{24} \cdot 32H_2O$ crystallises in pseudoregular octahedra and is isomorphous with the corresponding aluminium and chromium oxalates. $Rb_3Na_3Co_2(C_2O_4)_6 \cdot 5H_2O$ is monoclinic and isomorphous with the corresponding aluminium oxalate [$a:b:c=1.2211:1.08758$; $\beta=91^{\circ}38'$]. The crystals of $(NH_4)_3Na_3Co_2(C_2O_4)_6 \cdot 7H_2O$ are monoclinic, but so strongly striated that they cannot be measured.

E. W. W.

Ethyl Dioximidosuccinate. ANDRÉ WAHL (*Compt. rend.*, 1906, 143, 56—58).—Ethyl dioximidosuccinate, prepared by the action of hydroxylamine hydrochloride on ethyl dioxysuccinate (Anschütz and Parlato, *Abstr.*, 1892, 1181), is dimorphous, crystallising from a mixture of ether and light petroleum in small, transparent prisms, and in large, transparent crystals which become opaque and white when removed from the mother liquor; the two modifications melt and decompose at 196° and are mutually convertible by the action of solvents. It is soluble in boiling water, alcohol, or ether, and insoluble in cold water, and differs from the compound described by Beckh (*Abstr.*, 1897, i, 213), which is soluble in water and melts at 162° . Ethyl glyoxime-peroxide-dicarboxylate, $C_8H_{10}O_6N_2$, is obtained together with a little ethyl dinitroacetate when ethyl dioximidosuccinate is oxidised with fuming nitric acid, and when treated with ammonia yields the amide, $(CONH)_4$, melting at 250° (compare Präpper, *Abstr.*, 1883, 573; Cramer, *Abstr.*, 1892, 699; and Bouveault and Bongert, *Abstr.*, 1903, i, 145).

Ethyl 4-isonitrosoisooxazolone-3-carboxylate,



formed as a by-product in the above preparation of ethyl dioximidosuccinate, crystallises in white leaflets, melts and decomposes at $160\text{--}165^{\circ}$, is sparingly soluble in water, and yields a characteristic fugitive violet coloration with alkalis.

M. A. W.

Electrolytic Decomposition of Dicarboxylic Acids: Adipic Acid. B. LINO VANZETTI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 574—578. Compare *Abstr.*, 1904, i, 141).—In the electrolysis of potassium adipate, a large quantity of carbon dioxide is evolved at the anode, so that the decomposition of the acid is far more profound than has been formerly supposed. The mean and almost constant composition of the gases is: carbon dioxide, 25; unsaturated hydrocarbons,

1.5; oxygen, 12; carbon monoxide, 1.5; and hydrogen, 60 per cent. The unsaturated hydrocarbons consist of butylenes of the formulæ $\text{CH}_2\text{Me}\cdot\text{CH}\cdot\text{CH}_2$ and $\text{CHMe}\cdot\text{CHMe}$. The characteristic ethereal odour is due to the secondary formation of alcohols and ethereal salts.

T. H. P.

β -Methylglutaconic Acids. FRITZ FICHTER and JULIUS SCHWAB (*Annalen*, 1906, **348**, 251—256. Compare Feist, this vol., i, 334).—The action of ethyl β -chlorocrotonate or ethyl β -chloroisocrotonate on ethyl sodiomalonate leads to the formation of ethyl β -methyl-carboxyglutaconate, which boils at $163\text{--}165^\circ$ under 12 mm. pressure, and on hydrolysis with barium hydroxide yields a mixture of *cis*- and *trans*- β -methylglutaconic acids. The *cis*-acid melts at 152° , has a dissociation constant $K=0.0129$, and forms salts which crystallise more readily than do those of the *trans*-acid, which melts at 116° , has the dissociation constant $K=0.0139$, and is converted partially into the *cis*-form when boiled with aqueous sodium hydroxide (compare Feist, *loc. cit.*). Barium *trans*- β -methylglutaconate crystallises with $5\text{H}_2\text{O}$ ($6\text{H}_2\text{O}$; Genvresse, *Ann. Chim. Phys.*, 1891, [vi], **24**, 88). The *anilide* of the *trans*-acid, $\text{C}_{12}\text{H}_{11}\text{O}_2\text{N}$, melts at 166° and boils at 186° under 14 mm. pressure; the *p*-toluidide, $\text{C}_{13}\text{H}_{13}\text{O}_2\text{N}$, crystallises in long needles, melts at 164° , and boils at $236\text{--}240^\circ$ under 15 mm. pressure.

$\alpha\beta$ -Dibromo- β -methylglutaric acid, $\text{C}_6\text{H}_8\text{O}_4\text{Br}_2$, formed by the action of bromine under the influence of sunlight on *trans*- β -methylglutaconic acid dissolved in a mixture of glacial acetic acid and chloroform, crystallises from a mixture of chloroform and light petroleum and melts at 145° .

G. Y.

Condensation of Ethyl $\beta\beta$ -Dimethylglycidate with Ethyl Sodiomalonate. Synthesis of Terebic and Pyroterebic Acids. ALBIN HALLER and GUSTAVE BLANC (*Compt. rend.*, 1906, **142**, 1471—1473).— $\gamma\gamma$ -Dimethyl- $\alpha\beta$ -dicarbethoxybutyrolactone (4-methyl-2:3-dicarbethoxypentan-4-olid),
$$\begin{array}{c} \text{CO}_2\text{Et}\cdot\text{CH}\text{---}\text{CO} \\ | \\ \text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{CMe}_2 \end{array} > \text{O}$$
, obtained by the condensation of ethyl $\beta\beta$ -dimethylglycidate (Darzens, *Abstr.*, 1905, i, 116) with ethyl sodiomalonate, boils at 174° under 12 mm. pressure, crystallises from a mixture of ether and light petroleum in large prisms, melts at 46° , and is converted quantitatively into terebic acid by boiling with hydrochloric acid. The terebic acid was characterised by its conversion into pyroterebic acid and isohexolactone by the action of heat; the phenylhydrazide of pyroterebic acid melts at 106° .

Attempts to effect the condensation of ethyl $\alpha\beta\beta$ -trimethylglycidate with ethyl sodiomalonate were unsuccessful, owing probably to steric hindrance.

M. A. W.

Organic Thio-acids. II. EINAR BIILMANN (*Annalen*, 1906, **348**, 120—132. Compare *Abstr.*, 1905, i, 625; Holmberg, *Abstr.*, 1905, i, 323; Klason and Carlson, this vol., i, 232).—Thioglycollic acid is prepared by dissolving xanthoacetic acid in cooled 25 per cent. aqueous ammonia; after twenty-four hours, the mixture is extracted with ether

and heated at 112° , made alkaline with ammonia, and again extracted with ether and left overnight in contact with zinc filings; it boils at $103\text{--}105^{\circ}$ under 14 mm. pressure, and has a sp. gr. 1.326 at 17.3° .

Thiolactic acid is prepared from α -xanthopropionic acid; it boils at $98.5\text{--}99^{\circ}$ under 14 mm. pressure, and, when cooled with ice-water, crystallises, melting at about 10° .

Thiohydraerylic acid, prepared from β -xanthopropionic acid, forms white crystals, melts at 16.8° , boils at $110.5\text{--}111.5^{\circ}$ under 15 mm. pressure, decomposes when heated under the ordinary pressure, and has a sp. gr. 1.218 at 20.8° .

α -Xanthoisobutyric acid, $\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$, prepared from potassium xanthate and sodium isobutyrate, forms white crystals and melts at $102\text{--}103^{\circ}$. When heated with ammonia, it yields α -thiolisobutyric acid, which is crystalline, melts at 47° , boils at $101\text{--}102^{\circ}$ under 15 mm. pressure, gives an intense indigo-blue coloration with ferric chloride, changing to reddish-violet on addition of ammonia, forms with copper sulphate a yellow, with mercuric chloride or silver nitrate a white precipitate, and is oxidised by iodine, forming α -dithiodiisobutyric acid, $\text{C}_5\text{H}_{14}\text{O}_4\text{S}_2$, separating from hot water in colourless crystals.

Disulphidedisuccinic acid, $\text{S}_2[\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}]_2$, prepared by the oxidation of thiomalic acid with ferric sulphate and aqueous ammonia, is obtained as a white, crystalline residue. G. Y.

Organic Thio-acids. III. EINAR BIILMANN (*Annalen*, 1906, **348**, 133—143. Compare preceding abstract; Abstr., 1905, i, 625).—A reply to Holmberg (Abstr., 1905, i, 324).

Trithiocarbodiglycollic acid is formed by the action of sodium chloroacetate on potassium xanthate in hot aqueous solution or by heating alkali xanthoacetates with water. It is decomposed to only a small extent when boiled with water. The sodium salt crystallises with $2\frac{1}{2}\text{H}_2\text{O}$.

Carbethoxythioglycollic acid, $\text{OEt}\cdot\text{CO}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, prepared by the action of potassium thiocarbonate on potassium xanthate, forms colourless, transparent crystals, melts at $28\text{--}29^{\circ}$, boils at $110\text{--}115^{\circ}$ under 20 mm. pressure, is extremely hygroscopic, and is decomposed by alcoholic potassium hydroxide, yielding alcohol, carbon dioxide, and thioglycollic acid, or by alcoholic ammonia, yielding thioglycollic acid and xanthamide. The potassium salt, $\text{C}_5\text{H}_7\text{O}_4\text{SK}$, was analysed.

The action of ammonia on xanthoacetic acid leads to the formation of xanthamide, that of aniline to the formation of xanthanilide and *s*-diphenylcarbamide.

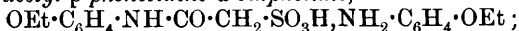
The formation of the reddish-yellow, crystalline potassium trithiocarbonate, $\text{C}_3\text{H}_2\text{O}_2\text{S}_3\text{K}_6$, by the successive action of hydrogen sulphide and carbon disulphide on alcoholic potassium hydroxide is confirmed.

G. Y.

Sulphoacetic Acid. II. Sulphoacetic Acid and Aromatic Amines. OTTO STILLICH (*J. pr. Chem.*, 1906, [ii], **74**, 51—56. Compare this vol., i, 552).—Aniline sulphoacetate, $(\text{NH}_2\text{Ph})_2\text{C}_2\text{H}_4\text{O}_6\text{S}$, formed by the action of aniline on aniline hydrogen sulphoacetate, melts at

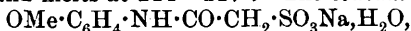
125—151°, decomposes into aniline and sulphoacetic acid when recrystallised from alcohol, and when highly heated yields *aniline acetanilide- ω -sulphonate*, $\text{NHPh}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}\cdot\text{NH}_2\text{Ph}$, which is formed quantitatively by heating aniline with sulphoacetic acid at 200°; it crystallises from absolute alcohol in long prisms and melts at 229—231°. The *sodium* salt, $\text{NHPh}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}\cdot\text{H}_2\text{O}$, forms nacreous, quadratic leaflets and melts at 283—284°.

p-Phenetidine sulphoacetate, $(\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_2\cdot\text{C}_2\text{H}_4\text{O}_5\text{S}$, crystallises in long, white needles, melts at about 146°, forming a turbid liquid which becomes clear at about 170°, and when highly heated forms *p*-phenetidine acetyl-*p*-phenetidine- ω -sulphonate,



this crystallises in needles, commences to sinter at 224°, and melts at 233—240°. The *sodium* salt, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}\cdot 2\text{H}_2\text{O}$, crystallises in needles and melts at about 270°, forming a turbid liquid which is not clear at 290°.

p-Anisidine acetyl-*p*-anisidine- ω -sulphonate forms matted needles, sinters at 220°, and melts at 224—227°. The *sodium* salt,



crystallises in nacreous, rectangular leaflets, commences to soften at about 269°, and gradually decomposes when more highly heated.

The salt, $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}\cdot\text{NH}_2\cdot\text{C}_7\text{H}_7$, formed from *o*-toluidine, crystallises in blue, pointed needles, melting at 189—191°; the *sodium* salt, $\text{C}_9\text{H}_{10}\text{O}_4\text{SNa}\cdot\text{H}_2\text{O}$, forms prismatic needles and melts at 223—224°.

The salt, $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}\cdot\text{C}_{10}\text{H}_7\cdot\text{NH}_2$, formed from *a*-naphthylamine, decomposes on recrystallisation; the *sodium* salt, $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}$, forms matted needles and melts at 285—287°.

G. Y.

Preparation of Aldehydes and Ketones from Alcohols.

W. LANG (D.R.-P. 166357).—The manganic salts are found to be very useful in oxidising alcohols to aldehydes and ketones, inasmuch as the reaction is not carried further when the oxidising agent is in excess.

Manganous ammonium sulphate, $2\text{MnSO}_4\cdot(\text{NH}_4)_2\text{SO}_4$, obtained in anhydrous crystals by adding excess of ammonium sulphate to a hot acid solution of manganous sulphate, is decomposed by cold water into the double sulphate, $\text{MnSO}_4\cdot(\text{NH}_4)_2\text{SO}_4$, and manganous sulphate, but when electrolysed in an anode cell lined with lead, the current density being 3.5 amperes per sq. cm., it gives rise to manganic ammonium alum, which is hydrolysed by water, yielding manganic hydroxide.

The mixture thus obtained is employed in oxidising methyl alcohol to formaldehyde, 2.4 parts of the latter being obtained from 4 parts of the alcohol. In a similar manner, 17 parts of menthol yield 14 parts of menthone.

G. T. M.

Decomposition of Formaldehyde by the Silent Discharge.

FRANZ RUSS (*Zeit. Elektrochem.*, 1906, 12, 412—413).—The silent discharge was passed through the vapour of formaldehyde at 150° and the formation of carbon monoxide and hydrogen observed.

T. E.

Preparation of a Solid Modification of Chloral. SIMON GÄRTNER (D.R.-P. 170534).—Chloral hydrate is left for several hours in contact with about half its weight of concentrated sulphuric acid until a white, pasty mass is formed. The acid is then poured off and the residue introduced into well-cooled dilute hydrochloric or sulphuric acid; the product, which now becomes solid, is washed and dried over concentrated sulphuric acid. This product can also be obtained from chloral alcoholate; it is only sparingly soluble in water and becomes quite insoluble when acid is added. It can be employed as an anæsthetic or a hypnotic, and, unlike chloral hydrate, it is devoid of any irritating action on the mucous membrane of the stomach.

G. T. M.

Preparation of Aldehydes, Alcohols, and Acids. CHEMISCHE FABRIK FLÖRSHEIM, H. HOERDLINGER (D.R.-P. 167137).—The volatile product obtained by blowing air, oxygen, or an ozonised mixture of these gases through heated oils or fats consists of a mixture of the lower aldehydes, alcohols, and aliphatic acids (from C_6 onwards).

Castor oil was heated to 160° and a current of air introduced; a vigorous reaction ensued, raising the temperature to 220° ; the distillate was collected and the oily portion mixed with petroleum and sodium hydrogen sulphite solution and saturated with sulphur dioxide until two clear layers separated. The petroleum extract when shaken with dilute aqueous sodium hydroxide yielded sodium *n*-hexoate and *n*-heptoate, and *n*-heptyl and *n*-octyl alcohols. The sodium hydrogen sulphite solution furnished heptaldehyde.

Similar results were obtained with linseed and rape-seed oils.

G. T. M.

Formation of Glycerose. NAZARENO TARUGI (*Gazzetta*, 1906, 36, i, 332—347. See this vol., ii, 631).

[Alkylenediamine Chromium Compounds.] PAUL PFEIFFER (*Annalen*, 1906, 346, 26—81. See this vol., ii, 614).

Antimonichlorides of Dichloro-salts. PAUL PFEIFFER and M. TAPUACH (*Zeit. anorg. Chem.*, 1906, 49, 437—440. Compare Abstr., 1904, ii, 41).—With the object of elucidating the constitution of the green double chloride of antimony and chromium, $CrCl_3 \cdot SbCl_5 \cdot 10H_2O$, described by Weinland and Feige (Abstr., 1903, ii, 218), the authors have prepared and examined two complex antimonichlorides of analogous constitution. The compound, $[Cr, C_4H_8N_2H_2 \cdot Cl_2][SbCl_5]$, prepared by the action of antimony pentachloride on violet *cis*-dichlorodiethylenediamine chromium chloride, $[Cr, C_4H_8N_2H_2 \cdot Cl_2]Cl$, dissolved in hydrochloric acid, forms violet crystals. The compound, $[Co \cdot C_4H_8N_2H_2 \cdot Cl_2][SbCl_5]$, obtained in a similar manner from *trans*-dichlorodiethylenediamine cobalt chloride, $[Co \cdot C_4H_8N_2H_2 \cdot Cl_2]Cl$, and antimony pentachloride, forms a green precipitate. The antimony was removed from these double salts by treatment with hydrogen sulphide, and from the respective filtrates derivatives of chromium and cobalt containing two atoms of chlorine were obtained, which proves the constitu-

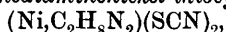
tion to be as above. From analogy, the formula $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2][\text{SbCl}_5]$ is ascribed to the double chloride of antimony and chromium in agreement with Weinland and Schmid (Abstr., 1905, ii, 326). G. S.

Compounds of Metallic Thiocyanates with Organic Bases

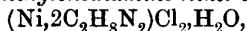
HERMANN GROSSMANN and BERNHARD SCHÜCK (*Zeit. anorg. Chem.*, 1906, 50, 1—20. Compare this vol., i, 7, 485).—In the present paper, compounds of ethylenediamine with thiocyanates and other salts of bivalent metals are described, and one or two compounds containing α - and β -naphthylamine have also been prepared. In the majority of cases the compounds were obtained by the direct action of the calculated quantity of base on the salt in aqueous solution; in some cases double decomposition between potassium thiocyanate and the ethylenediamine compound of other salts has been employed. In the course of the investigation it was found that, contrary to Ostwald's opinion (Abstr., 1886, 586), free ethylenediamine, and in some cases the combined base, can be accurately estimated by titration with sulphuric acid, using methyl-orange or litmus as indicator.

Nickel Compounds.—*Triethylenediaminenickel thiocyanate*,
 $(\text{Ni}, 3\text{C}_2\text{H}_8\text{N}_2)(\text{SCN})_2$,

separates from aqueous solution in violet, prismatic crystals, which melt at 253° . It is decomposed by acids with formation of the corresponding salt of ethylenediamine, and by hot potassium hydroxide, green nickel hydroxide being precipitated. *Diethylenediaminenickel thiocyanate*, $(\text{Ni}, 2\text{C}_2\text{H}_8\text{N}_2)(\text{SCN})_2$, has already been obtained by Werner (Abstr., 1899, i, 857) in two isomeric forms, which crystallise with H_2O in bluish-violet plates and in reddish-violet needles respectively. The authors confirm Werner's results except that their compounds are anhydrous; both melt at 220° . The nature of the isomerism has not been elucidated. *Ethylenediaminenickel thiocyanate*,



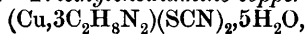
forms bluish-green, rhombic crystals, which melt at 275° . It is also decomposed by hot potassium hydroxide, but is not affected by ammonia. *Triethylenediaminenickel cyanide*, $(\text{Ni}, 3\text{C}_2\text{H}_8\text{N}_2)(\text{CN})_2$, prepared by the action of the molecular quantity of solid potassium cyanide on the corresponding thiocyanate, forms reddish-violet crystals, which melt at 244° . *Diethylenediaminenickel chloride*,



occurs in light blue, prismatic crystals, which melt at 157° . The triethylenediamine compound has already been prepared by Werner and Spruck (*loc. cit.*); attempts to obtain the mono-compound were unsuccessful.

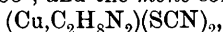
Zinc and Cadmium Compounds.—*Triethylenediamine zinc thiocyanate*, $(\text{Zn}, 3\text{C}_2\text{H}_8\text{N}_2)(\text{SCN})_2$, forms colourless, rhombohedric crystals, which melt at 161° . The corresponding *cadmium* compound, $(\text{Cd}, 3\text{C}_2\text{H}_8\text{N}_2)(\text{SCN})_2$, forms colourless plates which melt at 138° . No other compounds of these metals were obtainable.

Copper Compounds.—The three thiocyanates were obtained by double decomposition. *Triethylenediamine copper thiocyanate*,

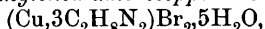


crystallises in large, deep blue plates, which melt at 138° . The

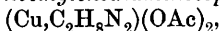
diethylenediamine compound, $(\text{Cu}, 2\text{C}_2\text{H}_8\text{N}_2)(\text{SCN})_2, 2\text{H}_2\text{O}$, forms dark blue needles, melting at 83° , and the *mono*-compound,



slender, light blue needles. The three compounds just mentioned are not affected by potassium hydroxide or by ammonia. *Ethylenediamine-copper chloride*, $(\text{Cu}, \text{C}_2\text{H}_8\text{N}_2)\text{Cl}_2, \text{H}_2\text{O}$, crystallises in reddish-blue leaflets which melt at 158° . With excess of hydrogen chloride, it yields the double *chloride*, $(\text{Cu}, \text{C}_2\text{H}_{10}\text{N}_2)\text{Cl}_4$, in golden-yellow leaflets melting at 272° . *Triethylenediaminecopper bromide*,



forms dark blue, lustrous leaflets, the *diethylenediamine* compound, $(\text{Cu}, 2\text{C}_2\text{H}_8\text{N}_2)\text{Br}_2, 2\text{H}_2\text{O}$, dark blue, prismatic crystals, and the *monoethylenediamine* compound, $(\text{Cu}, \text{C}_2\text{H}_8\text{N}_2)\text{Br}_2, \text{H}_2\text{O}$, lustrous, green plates. *Triethylenediaminecopper acetate*, $(\text{Cu}, 3\text{C}_2\text{H}_8\text{N}_2)(\text{OAc})_2, 2\text{H}_2\text{O}$, crystallises in dark blue leaflets, melting at 67° ; *diethylenediamine-copper acetate*, $(\text{Cu}, 2\text{C}_2\text{H}_8\text{N}_2)(\text{OAc})_2, \text{H}_2\text{O}$, in light blue, rhombic prisms, melting at 115° ; and *monoethylenediaminecopper acetate*,

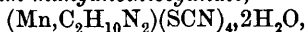


in dark green, lustrous, prismatic crystals. *Monoethylenediaminecopper sulphate*, $(\text{Cu}, \text{C}_2\text{H}_8\text{N}_2)\text{SO}_4, 3\text{H}_2\text{O}$, forms slender, light blue needles, which decompose on heating to 260° . *Diethylenediaminecopper nitrate*, $(\text{Cu}, 2\text{C}_2\text{H}_8\text{N}_2)(\text{NO}_3)_2, 2\text{H}_2\text{O}$, forms lustrous, dark blue leaflets and melts at 213° .

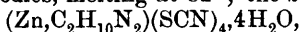
Attempts were made to prepare additive compounds with α - and β -naphthylamine, but only nickel compounds were obtained. *α -Naphthylaminenickel thiocyanate*, $(\text{Ni}, \text{C}_{10}\text{H}_9\text{N})(\text{SCN})_2$, separates from an alcoholic solution of its components as a moss-green, crystalline precipitate, which decomposes on heating above 200° . The β -compound forms a yellowish-green, crystalline precipitate, which melts about 261° .
G. S.

Ethylenediammonium Double Salts. HERMANN GROSSMANN and BERNHARD SCHÜCK (*Zeit. anorg. Chem.*, 1906, 50, 21—32. Compare Kurnakoff, *Abstr.*, 1898, ii, 475).—These double salts are of the general type $(\text{M}, \text{C}_2\text{H}_{10}\text{N}_2)\text{X}_4$, where M is a bivalent metal and X a univalent acid group, and have been prepared either by interaction of the salt of ethylenediamine with the corresponding salt of the metal in aqueous solution, or by dissolving the ethylenediamine additive compound (see preceding abstract) in excess of the corresponding acid.

Ethylenediammonium manganothiocyanate,



occurs in long, colourless plates which melt at 186° . The corresponding *ferrous* compound, $(\text{Fe}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SCN})_4, 4\text{H}_2\text{O}$, forms long, brown needles which become oxidised in the air; the *nickel* compound, $(\text{Ni}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SCN})_4, 4\text{H}_2\text{O}$, occurs in green, prismatic crystals and melts at 95° ; the *cobalt* compound, $(\text{Co}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SCN})_4, 2\text{H}_2\text{O}$, in slender, dark blue needles, melting at 82° ; the *zinc* compound,



in slender, colourless needles melting at 123° ; and the *cadmium* compound, $(\text{Cd}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SCN})_4$, in large, colourless, octahedral crystals which melt at 182° .

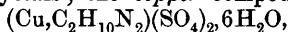
Ethylenediammonium mercurithiocyanate, $(\text{Hg}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SCN})_4$, forms colourless, prismatic crystals, which melt at 120° . The compound, $(\text{Hg}_2, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SCN})_6$, also forms colourless crystals which melt about 114° .

Ethylenediammonium cobaltchloride, $(\text{Co}, \text{C}_2\text{H}_{10}\text{N}_2)\text{Cl}_4 \cdot 6\text{H}_2\text{O}$, separates from aqueous solution in lustrous, light green needles which melt at 254° . The corresponding *bromide*, $(\text{Co}, \text{C}_2\text{H}_{10}\text{N}_2)\text{Br}_4 \cdot 2\text{H}_2\text{O}$, occurs in slender, light blue needles. *Ethylenediammonium cupribromide*, $(\text{Cu}, \text{C}_2\text{H}_{10}\text{N}_2)\text{Br}_4 \cdot 5\text{H}_2\text{O}$, occurs in black, lustrous leaflets which melt at 242° .

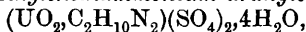
Ethylenediammonium cadmium chloride, $(\text{Cd}, \text{C}_2\text{H}_{10}\text{N}_2)\text{Cl}_4$, crystallises in colourless, four-sided plates, which melt and decompose at 300° ; the corresponding *bromide*, $(\text{Cd}, \text{C}_2\text{H}_{10}\text{N}_2)\text{Br}_4$, occurs in colourless, columnar crystals which decompose about 190° .

Ethylenediammonium uranyl chloride, $(\text{UO}_2, \text{C}_2\text{H}_{10}\text{N}_2)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$, forms yellow, prismatic crystals, which are very hygroscopic and melt about 219° .

Ethylenediammonium ferrous sulphate, $(\text{Fe}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, occurs in light green, tabular crystals; *ethylenediammonium cobalt-sulphate*, $(\text{Co}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, in rose-coloured, triclinic crystals; and *ethylenediammonium manganosulphate*, $(\text{Mn}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, in faintly rose-coloured crystals. *Ethylenediammonium nickelosulphate*, $(\text{Ni}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, forms green, triclinic crystals; the corresponding *cadmium* compound, $(\text{Cd}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, occurs in colourless, triclinic crystals; the *copper* compound,



in monoclinic crystals; the *zinc* compound, $(\text{Zn}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, in colourless, monoclinic crystals; and the *magnesium* compound, $(\text{Mg}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, in small, colourless needles. *Ethylenediammonium aluminosulphate*, $(\text{Al}_2, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_4 \cdot 4\text{H}_2\text{O}$, occurs in colourless leaflets. *Ethylenediammonium uranylosulphate*,

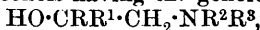


forms small, light yellow, six-sided crystals, which decompose above 285° ; *ethylenediammonium uranylnitrate*, $(\text{UO}_2, \text{C}_2\text{H}_{10}\text{N}_2)(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$, forms greenish-yellow, four-sided, columnar crystals, which melt about 215° and are strongly fluorescent. The double uranyl nitrate acts on the photographic plate, whilst the double sulphate and chloride have no action on it; on the other hand, the electroscope is affected about equally by the nitrate and the sulphate. The crystals of the double sulphates described in this paragraph have been measured and the results are tabulated.

Attempts were made to obtain double sulphates containing ethylamine, but only the zinc compound was obtained. *Ethylammonium zinc sulphate*, $(\text{Zn}, 2\text{C}_2\text{H}_5\text{N})(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$, obtained by interaction of ethylamine sulphate and zinc sulphate in aqueous solution, occurs in large, colourless crystals.

G. S.

Preparation of Aminoalcohols. J. D. RIEDEL (D.R.-P. 169746, 169819).—The aminoalcohols having the general formula



where R, R¹, R², and R³ are alkyl or aryl groups, are substances which

may be employed in the production of anæsthetics. The halogen hydrins required for the preparation of these aminoalcohols are readily obtained from chloroacetone and its analogues by the Grignard reaction. The following carbinols were thus obtained for the first time :

Methylchloromethylpropylcarbinol, $\text{CH}_2\text{Cl}\cdot\text{CMePr}\cdot\text{OH}$, boiling at 75° under 35 mm. pressure; *methylchloromethylisobutylcarbinol*, $\text{CH}_2\text{Cl}\cdot\text{CMe}(\text{C}_4\text{H}_9)\cdot\text{OH}$, boiling at 85° under 25 mm. pressure; *methylchloromethylisoamylcarbinol*, $\text{CH}_2\text{Cl}\cdot\text{CMe}(\text{C}_5\text{H}_{11})\cdot\text{OH}$, boiling at $96\text{--}98^\circ$ under 23 mm. pressure; *benzylmethylchloromethylcarbinol*, $\text{CH}_2\text{Cl}\cdot\text{CMe}(\text{C}_7\text{H}_7)\cdot\text{OH}$, boiling at 155° under 25 mm. pressure; *chloromethyldiethylcarbinol*, $\text{CH}_2\text{Cl}\cdot\text{CEt}_2\cdot\text{OH}$, boiling at 88° under 35 mm. pressure.

Dimethylaminomethyldiethylcarbinol, $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CEt}_2\cdot\text{OH}$, obtained by the action of dimethylamine on the last of these chlorohydrins at 130° , is a colourless liquid boiling at $76\text{--}79^\circ$ under 23 mm. pressure; the *hydrochloride* of its *benzoyl* derivative crystallises from alcohol in well-defined, lustrous plates melting at 189° .

Dimethylaminodimethylethylcarbinol, $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CMeEt}\cdot\text{OH}$, is a colourless liquid boiling at 57° under 23 mm. pressure; the *hydrochloride* of its *benzoyl* derivative melts at 175° .

Dimethylaminodimethylpropylcarbinol, $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CMePr}\cdot\text{OH}$, boils at 78° under 35 mm. pressure; its salts are not crystallisable, but the *hydrochloride* of its *benzoyl* derivative separates in very soluble hygroscopic needles melting at 146° .

Dimethylaminodimethylisobutylcarbinol boils at 82° under 34 mm. pressure, the *hydrochloride* of the *benzoyl* derivative melts at 134° .

Dimethylaminodimethylisoamylcarbinol boils at $98\text{--}99^\circ$ under 24 mm. pressure; the *hydrochloride* of the *benzoyl* derivative forms silky needles and melts at 138° .

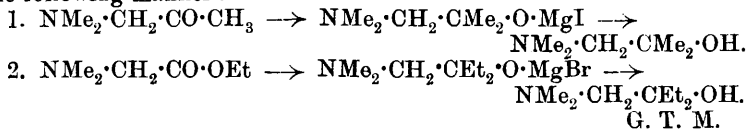
Phenylmethylaminodimethylcarbinol, $\text{NHMe}\cdot\text{CH}_2\cdot\text{CMePh}\cdot\text{OH}$, boils at $135\text{--}138^\circ$ under 31 mm. pressure; its *hydrochloride* melts at 153° and its *dibenzoyl* derivative at 122° .

Phenyldimethylaminodimethylcarbinol, $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CMePh}\cdot\text{OH}$, boils at $135\text{--}136^\circ$ under 32 mm. pressure; its *hydrochloride* melts at $159\text{--}160^\circ$.

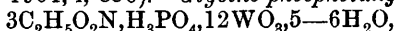
Phenyldiethylaminodimethylcarbinol, $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CMePh}\cdot\text{OH}$, is a viscid liquid boiling at $147\text{--}149^\circ$ under 24 mm. pressure.

Benzyl dimethylaminodimethylcarbinol, $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{C}_7\text{H}_7)\cdot\text{OH}$, boils at 144° under 24 mm. pressure, the *hydrochloride* of its *benzoyl* derivative melts at 195° .

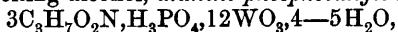
This series of aminoalcohols can also be prepared by applying the Grignard reaction to the dialkyl-aminoacetones and -aminoesters in the following manner :



Phosphotungstates of some Amino-acids. M. BARBER (*Monatsh.*, 1906, 27, 379—401. Compare Gulewitsch, *Abstr.*, 1899, i, 833; Schulze and Winterstein, *Abstr.*, 1902, i, 137; Grossmann and Kraemer, *Abstr.*, 1904, i, 850).—*Glycine phosphotungstate*,



which crystallises in stout prisms and nodular aggregates, and is decomposed by boiling alcohol, *alanine phosphotungstate*,



which crystallises in microscopic, stout, pointed needles, *asparagine phosphotungstate*, $5C_4H_8O_3N_2, 2H_3PO_4, 22WO_3, 10H_2O$, and *aspartic acid phosphotungstate*, $4C_4H_7O_4N, 2H_3PO_4, 20-22WO_3, 24H_2O$, which crystallises in microscopic octahedra, are prepared by adding 50 per cent. phosphotungstic acid to the hot saturated aqueous solution of the amino-acid, or by dissolving the latter in the phosphotungstic acid solution, so that the proportion present is 1 amino-acid:10 phosphotungstic acid. These four phosphotungstates lose their water of crystallisation at 105°. The phosphotungstate of glycine is soluble to the extent of 4.5, 14.4, and 21.3, of alanine to the extent of 15.7, 19.4, and 27.6, of asparagine, 6.8, 66, and 400, and of aspartic acid, 3, 24, and 400, in water, absolute alcohol, and 80 per cent. alcohol, respectively.

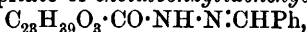
Glutamic acid and phosphotungstic acid yield products which have the approximate composition $C_5H_9O_4N, 3(H_3PO_4, 12WO_3)$, or, after recrystallisation from water, $3C_5H_9O_4N, 2(H_3PO_4, 12WO_3)$. These are isomorphous mixtures of the phosphotungstate and phosphotungstic acid, and on further recrystallisation from water yield other isomorphous mixtures of varying intermediate composition.

Crystalline phosphotungstates could not be obtained from tyrosine or leucine (compare Kossel and Kutscher, *Abstr.*, 1901, i, 107).

Various methods of separating phosphorus from tungstic acid in organic phosphotungstates are compared. Satisfactory results were obtained only with Sprenger's method (*Abstr.*, 1881, 140) when modified by precipitation of the phosphoric acid by means of ammonium molybdate, instead of ferric chloride and ammonium acetate.

G. Y.

Synthesis of Glycocholic and Taurocholic Acids. S. BONDI and ERNST MÜLLER (*Zeit. physiol. Chem.*, 1906, 47, 499—506).—Pure cholic acid melts at 198° and is most readily prepared by a modification of Mylius' method (*Abstr.*, 1888, 508). The ethyl ester melts at 162°. The *hydrazide*, $C_{23}H_{39}O_3 \cdot CO \cdot NH \cdot NH_2$, obtained by heating an alcoholic solution of the ester with hydrazine hydrate, crystallises from hot water in colourless, glistening needles containing water of crystallisation. The anhydrous compound melts at 188—189°, dissolves in most organic solvents, and reduces a cold ammoniacal silver nitrate solution. The solution of the hydrazide in dilute hydrochloric acid yields with benzaldehyde a precipitate of *cholalbenzylidenelhydrazine*,



The *azide* of cholic acid, $C_{23}H_{39}O_3 \cdot CON_3$, obtained by the action of nitrous acid on the hydrazide, is precipitated as a fine powder,

decomposes vigorously at 73° , is insoluble in water, but dissolves readily in alcohol or chloroform. The azide condenses with alkaline solutions of glycine and taurine, yielding respectively glyco- and taurocholic acids.

J. J. S.

Preparation of Bromodialkylacetamides. KALLE & Co. (D.R.-P. 170629).—Ethyl bromodiethylacetate when dissolved in alcohol and shaken for some time with aqueous ammonia yields bromodiethylacetamide, which can be recrystallised from light petroleum. This amide is also obtained by carefully heating ammonium bromodiethylacetate at 110° under diminished pressure; ammonium bromodipropylacetate can be converted similarly into bromodipropylacetamide.

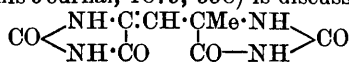
G. T. M.

Acyl Derivatives of Cyanamide and Carbamide. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 167138).—Cyanoacetic acid or the halogenated acetic acids interact readily with cyanamide or its monoalkyl derivatives. Chloroacetylmethylcarbamide results from the interaction of chloroacetic acid and methylcyanamide in ethereal solution.

Cyanoacetylmethylcarbamide, $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHMe}$, obtained in a similar manner from cyanoacetic acid and methylcyanamide, crystallises in colourless needles and melts at 206° .

G. T. M.

Action of Bromine on α -Lactylcarbamide and Related Compounds SIEGMUND GABRIEL (*Annalen*, 1906, 348, 50—90. Compare Abstr., 1905, i, 265; Fischer and Roeder, Abstr., 1902, i, 124; Andreasch, Abstr., 1903, i, 157).—The constitution of pyruvic ureide (Grimaux, this Journal, 1875, 358) is discussed, and



adopted as the most probable.

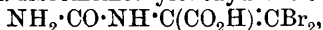
α -Methylhydantoin (α -lactylcarbamide) yields pyruvic ureide when heated with 1 mol. of bromine in aqueous solution in a sealed tube on the water-bath. When heated with 1 mol. of bromine in glacial acetic acid solution under varying conditions, it yields pyruvic ureide, α -bromomethylenehydantoin, and the *hydrobromide* of pyruvic ureide hydrate, $\text{C}_8\text{H}_{10}\text{O}_5\text{N}_4\cdot\text{HBr}$; this crystallises in flat, stout, short prisms, sinters at about 205° , and melts and decomposes at 210 — 211° . When treated with water, it is converted into *pyruvic ureide hydrate*, $\text{C}_8\text{H}_{10}\text{O}_5\text{N}_4\cdot 2\text{H}_2\text{O}$, which forms glistening, flat needles, loses $2\text{H}_2\text{O}$ at 100° , sinters and becomes yellow at 233° , melts and decomposes at 243 — 244° , and yields pyruvic ureide when heated with concentrated sulphuric acid and diluted with water.

α -Bromomethylenehydantoin, $\text{CO} \begin{array}{c} \text{NH}\cdot\text{C}\cdot\text{CHBr} \\ \text{NH}\cdot\text{CO} \end{array}$, is formed also by the action of 2 mols. of bromine on α -methylhydantoin in glacial acetic acid solution on the water-bath; it crystallises in slightly yellow needles, melts and decomposes at 241 — 242° , and is reduced to α -methylhydantoin by fuming hydriodic acid.

The action of 3 mols. of bromine on α -methylhydantoin in glacial

acetic acid solution leads to the formation of α -dibromomethylenehydantoin (Fischer, Abstr., 1887, 918), which is formed also by dissolving tribromopyruvylcarbamide (Fischer, *loc. cit.*) in concentrated sulphuric acid, and is reduced to α -methylhydantoin by hydriodic acid.

The action of bromine water on α -bromomethylenehydantoin leads to the formation of α -dibromomethylenehydantoic acid,



which melts and decomposes at 207° and is identical with Grimaux's dibromodihydromalonylcarbamide (*loc. cit.*), but, contrary to that author's statement, gives a brownish-yellow coloration with dilute ammonia. When heated with concentrated sulphuric acid at 80° , it is converted into α -dibromomethylenehydantoin. The *methyl* ester, $\text{C}_5\text{H}_8\text{O}_3\text{N}_2\text{Br}_2$, formed by heating the above acid with methyl alcohol and hydrogen chloride, crystallises in flat needles and melts at 208° .

When heated with α -bromomethylenehydantoin and hydrogen bromide in glacial acetic acid solution, α -methylhydantoin forms pyruvic ureide; the condensation does not take place in the absence of hydrogen bromide.

Dihydropyruvic ureide, $\text{C}_8\text{H}_{10}\text{O}_4\text{N}_4$, formed with development of heat when pyruvic ureide, or its hydrate, or the hydrobromide of the hydrate is reduced with fuming hydriodic acid, crystallises from boiling water in transparent, flat, pointed, white plates, becomes brown at about 282° , and melts and decomposes at 299° . When hydrolysed with barium hydroxide and water under pressure at 165° , it yields alanine, carbon dioxide, and ammonia; with hydrochloric acid at 165° , it yields ammonia and *dialanine*, $\text{CO}_2\text{H} \cdot \text{CH}(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{CMe}(\text{NH}_2) \cdot \text{CO}_2\text{H}$, which crystallises in thin, hexagonal leaflets or needles, melts and decomposes at 248 – 249° , forms a readily soluble crystalline *hydrochloride* and a *platinichloride*, is converted into dihydropyruvic ureide by the action of potassium cyanate in aqueous solution, and yields 4N when treated with an excess of barium nitrite and dilute sulphuric acid (Fischer and Koelker, Abstr., 1905, i, 692).

$\alpha\beta$ -Dimethylhydantoin, $\begin{array}{c} \text{CHMe} \cdot \text{NMe} \\ \text{CO} \text{---} \text{NH} \end{array} > \text{CO}$, is prepared by shaking

ethyl α -bromopropionate with aqueous methylamine, heating the resulting solution at 100° , evaporating with barium hydroxide, and, after removal of the barium as carbonate, treating the residue with potassium cyanate in aqueous solution. It crystallises in stout, colourless needles, melts at 120 – 121° , is readily soluble in water, alcohol, ethyl acetate, chloroform, or acetone, less so in ether, and is only sparingly soluble in light petroleum. When treated with 1 mol. of bromine in glacial acetic acid solution, it yields the *hydrobromide* of pyruvic dimethylureide hydrate, $\text{C}_8\text{H}_8\text{O}_5\text{N}_4\text{Me}_2 \cdot \text{HBr}$, which crystallises in needles, darkens at 200° , and melts and decomposes at 285° . *Pyruvic dimethylureide hydrate*, $\text{C}_8\text{H}_8\text{O}_5\text{N}_4\text{Me}_2$, crystallises in colourless, quadratic plates or scales, melts and decomposes at 255 – 256° , and is reduced by fuming hydriodic acid to *dihydropyruvic dimethylureide*, $\text{C}_8\text{H}_8\text{O}_4\text{N}_4\text{Me}_2$, which crystallises in colourless leaflets and melts at 275 – 277° .

The action of 2 mols. of bromine on $\alpha\beta$ -dimethylhydantoin in glacial acetic acid solution leads to the formation of β -methyl- α -bromo-

methylenehydantoin, $\text{CO} \begin{array}{c} \text{NMe} \cdot \text{C} \cdot \text{CHBr} \\ \text{NH} \cdots \text{CO} \end{array}$, which crystallises in pointed, yellow needles, melts at $143-144^\circ$, and is readily reduced by hydriodic acid.

α -Bromomethylenehydantoin and $\alpha\beta$ -dimethylhydantoin interact in presence of hydrogen bromide in glacial acetic acid solution, forming *pyruvic methylureide*, $\text{CO} \begin{array}{c} \text{NH} \cdot \text{C} \cdot \text{CH} \cdot \text{CMe} \cdot \text{NMe} \\ \text{NH} \cdot \text{CO} \quad \text{CO} \cdots \text{NH} \end{array} \text{CO}$, which crystallises in microscopic needles or prisms and melts and decomposes at about $299-300^\circ$.

α -Ethyl-lacturamic acid, $\text{NH}_2 \cdot \text{CO} \cdot \text{NEt} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$, prepared from ethylamine, ethyl α -bromopropionate, and potassium cyanate, forms rhombic crystals, melts and decomposes at 155° , and when evaporated with hydrochloric acid yields α -methyl- β -ethylhydantoin (Duvillier, Abstr., 1896, i, 89), which crystallises in rhombic plates and melts at 85° . This condenses with α -bromomethylenehydantoin in presence of hydrogen bromide in glacial acetic acid solution, forming *pyruvic ethylureide*, $\text{CO} \begin{array}{c} \text{NH} \cdot \text{C} \cdot \text{CH} \cdot \text{CMe} \cdot \text{NEt} \\ \text{NH} \cdot \text{CO} \quad \text{CO} \cdots \text{NH} \end{array} \text{CO}$, which crystallises in short, pointed prisms and melts and decomposes at 249° .

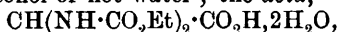
α -Ethylhydantoic acid, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CHEt} \cdot \text{CO}_2\text{H}$, prepared from ethyl α -bromobutyrate, ammonia, and potassium cyanate, crystallises in quadratic plates and melts and decomposes at 177° . α -Ethylhydantoin, $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CHEt} \\ \text{NH} \cdot \text{CO} \end{array}$, crystallises in leaflets, melts at $117-118^\circ$, and on bromination in glacial acetic acid solution yields α -bromoethylidenehydantoin, $\text{CO} \begin{array}{c} \text{NH} \cdot \text{C} \cdot \text{CBrMe} \\ \text{NH} \cdot \text{CO} \end{array}$, which forms rhombic leaflets and melts and decomposes at $230-236^\circ$.

Hydantoin is oxidised by bromine in glacial acetic acid solution, forming parabanic acid. The condensation of hydantoin with α -bromomethylenehydantoin in presence of hydrogen bromide in acetic acid solution leads to the formation of only a small amount of pyruvic ureide.

Malylureide (Guareschi, Abstr., 1878, 138), formed by the action of potassium cyanate on aspartic acid, melts and decomposes at $224-226^\circ$, and when treated with bromine in acetic acid solution yields the acid, $\text{CO} \begin{array}{c} \text{NH} \cdot \text{C} \cdot \text{CH} \cdot \text{CO}_2\text{H} \\ \text{NH} \cdot \text{CO} \end{array}$, which crystallises in rhombic leaflets, decomposes at $280-350^\circ$, forms crystalline *barium* and *silver* salts, is reduced to malylureide by fuming hydriodic acid, and on treatment with bromine water forms α -dibromomethylenehydantoic acid. G. Y.

Action of Urethane and of Carbamide on Ethyl Glyoxylate. New Synthesis of Allantoin. LOUIS J. SIMON and J. CHAVANNE (*Compt. rend.*, 1906, 143, 51-54. Compare this vol., i, 396).—*Ethyl diurethaneglyoxylate*, $\text{CH}(\text{NH} \cdot \text{CO}_2\text{Et})_2 \cdot \text{CO}_2\text{Et}$, obtained by the condensation of ethyl glyoxylate with urethane, crystallises in colourless, transparent prisms, melts at 143° , can be distilled under reduced pressure, dissolves in alcohol, acetic acid, or chloroform, and is stable

in boiling water. The *amide*, $\text{CH}(\text{NH}\cdot\text{CO}_2\text{Et})_2\cdot\text{CO}\cdot\text{NH}_2$, melts at 190° and is soluble in alcohol or hot water; the *acid*,



obtained from the ester by the action of aqueous or alcoholic potassium hydroxide, crystallises from boiling water in thin, silky needles, melts at $159\text{--}160^\circ$, and loses its water of crystallisation at $110\text{--}115^\circ$; the anhydrous acid melts at 165° . Diurethaneglyoxylic acid is much more stable than its higher homologue, diurethanepyrvic acid (this vol., i, 404); it is soluble in alcohol, forms crystalline salts with phenylhydrazine or the aromatic bases, reddens litmus, can be titrated in the presence of phenolphthalein, and is precipitated by mineral acids from a solution of its alkali salt.

Ethyl glyoxylate condenses with carbamide in the presence of hydrogen chloride to form *ethyl allantoate*, $\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_2\cdot\text{CO}_2\text{Et}$, a white, microcrystalline substance which decomposes at 200° . It is converted into allantoin by the action of ammonia or alkali hydroxides, and in this respect resembles its higher homologue, ethyl homoallantoate (Abstr., 1902, i, 15; 1904, i, 300), from which, however, it differs in its stability towards boiling water, which decomposes ethyl homoallantoate, whilst ethyl allantoate can be recrystallised from that solvent or from boiling alcohol; it is decomposed by acids, regenerating ethyl glyoxylate.

M. A. W.

Preparation of Aminoguanidine from Nitroguanidine. C. F. BOEHRINGER & SÖHNE (D.R.-P. 167637).—The electrolytic reduction of nitroguanidine with zinc and platinum electrodes gives unsatisfactory results, but when either a tin cathode is used or a tin salt or finely-divided tin is added to the solution, the yield of aminoguanidine is greatly increased. The nitro-compound is suspended in water slightly acidified with sulphuric acid. A tin cathode with roughened surface is employed and the current density is 250 amperes per sq. metre; the temperature is maintained at 10° , and during the electrolysis just sufficient acid is added from time to time to fix the amine which is being produced; the yield is 81 per cent. of the theoretical.

G. T. M.

Substances extracted from Muscle. III. Methylguanidine. WLADIMIR GULEWITSCH (*Zeit. physiol. Chem.*, 1906, 47, 471—475. Compare Abstr., 1900, i, 516; 1905, i, 726; also Kutscher, *Zeit. Nahr. Genussm.*, 1905, 10, 531).—Methylguanidine has been isolated from the extract of muscle. The nitrate of the base melts at 150° . The *picrate*, whether obtained from creatine or from muscle extract, crystallises from water in two distinct modifications: a yellow form crystallising in four- or six-sided pleochroic plates, and an orange-coloured form crystallising in short, four-cornered plates also showing pleochroism. When crystallised under certain conditions, each form can be partially transformed into the other. Guanidine picrate also crystallises in two distinct forms (von Cordier, this vol., i, 486).

J. J. S.

Action of Sulphides on Nitroprussides. JUAN F. VIRGILI (*Zeit. anal. Chem.*, 1906, 45, 409—439. Compare Abstr., 1902, ii, 472).—An attempt is made to explain the different colours produced on mixing solutions of sodium nitroprusside with soluble sulphides.

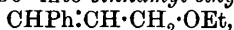
The reddish-yellow, red, purple, and violet shades which are obtained under different conditions are due to the simultaneous formation of two substances, one of which is blue and represents a molecular compound of the sulphide and the nitroprusside, whilst the other (a quaternary nitroprusside) is yellow and is formed by the action of alkali hydroxide on the normal nitroprusside. This view is supported by a study of the absorption spectra. In order to obtain the blue coloration, free alkali hydroxide and alkali salts of weak acids must be absent. It is readily produced when the nitroprusside is added to an excess of a concentrated solution of the sulphide in ethyl alcohol or glycerol, or to an aqueous solution containing excess of hydrogen sulphide. On account of the increasing hydrolysis, a larger excess of hydrogen sulphide is required with increasing dilution, and by reason of the weak basic character of ammonia the blue coloration is more readily obtained with ammonium sulphide than with the alkali metal sulphides. With solutions of the alkali hydrogen sulphides, the colour is distinctly more blue than with corresponding solutions of the normal sulphides. These facts are readily explained by the author's hypothesis.

Experiments on the mixing of solutions under different conditions indicate that the nitroprusside does not react with the sulphide ion but with the non-ionised sulphide. The intensity of the coloration increases when salts with a common ion are added to the solution or when solvents of smaller ionising power are used. The sensitiveness of the nitroprusside as a reagent for sulphide is considerably diminished in consequence of hydrolysis, and addition of substances which decrease the hydrolysis (alkali hydroxides) increases the sensitiveness. Low temperature also increases the sensitiveness; whilst at 20° sodium sulphide could be detected at a concentration of 0.0033 gram per litre, it was found that at 0° the colour change was given at a concentration of 0.0011 gram per litre. On account of the difficulty of obtaining comparable colorations, nitroprusside is not suitable for the estimation of hydrogen sulphide.

H. M. D.

Attempts to Synthesise Phenylallene. AUGUST KLAGES and KARL KLENK (*Ber.*, 1906, 39, 2552—2555).—Cinnamyl chloride, obtained from cinnamyl alcohol and hydrogen chloride in the cold, boils at 120° under 18 mm. pressure, has a sp. gr. 1.101 at 15°/4°, and, contrary to statements in the literature, forms a *dibromide* which melts at 104—105°. When heated with pyridine (2 mols.), it yields a *pyridinium chloride*, which is easily soluble in water and alcohol, and forms a yellow platinichloride and aurichloride, and a white mercurichloride.

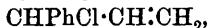
Cinnamyl bromide, C_9H_9Br , obtained from cinnamyl alcohol and hydrogen bromide in glacial acetic acid at 0°, melts at 34°, boils at 103° under 22 mm. pressure, forms with bromine long, white needles of $\alpha\beta$ -tribromo- α -phenylpropane, which melts at 128°, and is converted by alcoholic potash at 130° into *cinnamyl ethyl ether*,



a colourless oil which boils at 231—232°.

The reaction between magnesium phenyl bromide and acetaldehyde leads to the formation of *α -phenylallyl alcohol*, $OH \cdot CHPh \cdot CH \cdot CH_2$, an

oil which boils at 106° under 18 mm. and at 214° under 746 mm. pressure, has a sweet burning taste, and yields with excess of bromine the tribromide previously described. *α -Phenylallyl chloride*,



is a colourless oil with a strong odour; with bromine it forms an additive compound, $\text{C}_9\text{H}_9\text{ClBr}_2$, which melts at 104° .

α -Phenylallyl bromide is a colourless oil with an irritating vapour; it solidifies in ice and is converted by alcoholic potash at 120° into *α -phenylallyl ethyl ether*, $\text{CH}_2 : \text{CH} \cdot \text{CHPh} \cdot \text{OEt}$, an oil which has a faint fruity odour and boils at 203 — 205° under 755 mm. pressure. C. S.

Condensation Products of cyclopentadiene. JOHANNES THIELE and HANS BALHORN [in part with WALTHER ALBRECHT] (*Annalen*, 1906, 348, 1—15. Compare Thiele, Abstr., 1900, i, 298; this vol., i, 569, 586).—Methylethylfulvene (Engler and Frankenstein, Abstr., 1901, i, 658), prepared by the condensation of cyclopentadiene with methyl ethyl ketone in presence of sodium ethoxide in cooled alcoholic solution, boils at 62.5° under 13 mm. pressure, volatilises with ether vapour, gives a red coloration and a light precipitate with glacial acetic-sulphuric acid, and resinifies when exposed to air.

Diethylfulvene, $\begin{matrix} \text{CH} : \text{CH} \\ \text{CH} : \text{CH} \end{matrix} > \text{C} : \text{CEt}_2$, prepared in the same manner from

cyclopentadiene and diethyl ketone, boils at 74.5 — 78.5° under 19 mm. pressure and closely resembles dimethylfulvene in its colour, odour, and reactions.

A product, $\begin{matrix} \text{CH} : \text{CH} \\ \text{CH} : \text{CH} \end{matrix} > \text{C} : \text{C} < \begin{matrix} \text{CH}_2 \cdot \text{CMe}_2 \\ \text{CH}_2 \cdot \text{CMe}_2 \end{matrix} > \text{O}$, is formed together with

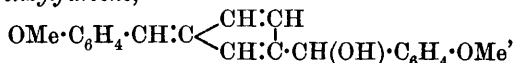
dimethylfulvene by the condensation of acetone with cyclopentadiene in alcoholic sodium ethoxide or concentrated methyl-alcoholic potassium hydroxide solution, or with dimethylfulvene in presence of alcoholic sodium ethoxide; it is obtained as a dark orange oil which boils at 110° under 11 mm. pressure.

Freshly-distilled dimethylfulvene solidifies quickly when cooled with ice, forming yellow crystals melting at about 4° , but after four to five months the oil solidifies only slowly and the yellow crystals change at the ordinary temperature into *bisdimethylfulvene*, $\text{C}_{16}\text{H}_{20}$, which crystallises from alcohol in hexagonal plates or needles, melts at 83° , yields dimethylfulvene when heated above its melting point, is not resinified by air, gives a yellowish-red coloration with concentrated sulphuric acid, reduces potassium permanganate immediately in alcoholic solution, and forms an additive compound with 2 mols. of bromine. *isoNitroso-dimethylfulvene*, $\text{C}_8\text{H}_8 : \text{CMe} \cdot \text{CH} : \text{NOH}$, prepared from *isonitrosoacetone* and cyclopentadiene, crystallises in glistening, reddish-brown needles or prisms, melts at 87° , has a characteristic odour, reduces ammoniacal silver and Fehling's solutions when heated, and is dissolved and decomposed by warm dilute sulphuric acid.

Cinnamylidenecyclopentene, $\text{C}_5\text{H}_4 : \text{CH} \cdot \text{CH} : \text{CHPh}$, formed by condensation of cyclopentadiene and cinnamaldehyde in presence of methyl-alcoholic potassium hydroxide, crystallises in bluish-red needles, melts at 102° , is rapidly oxidised by moist oxygen, gives a violet to blue

coloration with concentrated sulphuric acid, forms an *additive* compound with bromine, and is reduced by aluminium amalgam to an oil which readily resinifies.

The condensation of *cyclopentadiene* with anisaldehyde leads to the formation of *p*-methoxyphenylfulvene and *p*-methoxyphenyl- α -hydroxy-*p*-methoxybenzylfulvene,

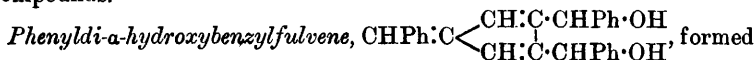


which crystallises in sheaves of red prisms, melts at 129°, is readily oxidised, and with concentrated sulphuric acid gives a deep blue coloration becoming red.

p-Methoxyphenylfulvene, $\text{C}_5\text{H}_4 : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, crystallises in short, red spears, melts at 70°, and gives an orange coloration with concentrated sulphuric acid.

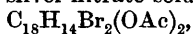
p-Methoxybenzylcyclopentene, $\text{C}_5\text{H}_5 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, formed by reduction of the last substance with aluminium amalgam in moist ether, is obtained as a light orange oil, which on cooling deposits a small amount of white crystals melting at 163°. The oil boils at 153—154° under 9 mm. pressure, and solidifies to glistening, colourless crystals melting at 53°. It forms an *additive* compound with bromine, and gives an orange coloration with concentrated sulphuric acid.

The yellow, insoluble condensation product of *cyclopentadiene* with formaldehyde contains a polymeride of fulvene together with oxygen compounds.



by the condensation of *cyclopentadiene* with benzaldehyde, crystallises in red needles, melts at 178—179°, absorbs bromine, and gives a violet coloration with concentrated sulphuric acid.

Diphenylfulvene dibromide, $\text{C}_{18}\text{H}_{14}\text{Br}_2$, crystallises in yellow plates, melts at 102—102.5°, and decomposes on exposure to air. The *tetrabromide*, $\text{C}_{18}\text{H}_{14}\text{Br}_4$, forms yellow plates, melts at 123°, dissolves in boiling aniline, alcohol, or glacial acetic acid, forming red solutions, gives a green coloration when reduced with zinc dust in chloroform or benzene, is decomposed by alcoholic alkali hydroxides, and forms silver bromide when heated with silver nitrate solution. The *diacetate*,



formed by boiling the tetrabromide with potassium acetate in glacial acetic acid solution, crystallises in white leaflets and melts at 166—167°. G. Y.

So-called Aromatic Substances containing Six Atoms of Carbon. GEORG KÖRNER (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 525—526).—In the chemistry of the halogen- and nitro-substitution products of benzene there are still many gaps, besides which many incorrect data have been published. The author proposes to fill up the gaps in, and revise generally, the knowledge of the formation and properties of aromatic compounds containing six carbon atoms, with a view to ascertaining the influence of the nature and position of each substituent atom or group of atoms on the ultimate properties of the molecule (compare following abstract). T. H. P.

The Sixth Dibromonitrobenzene. GEORG KÖRNER and ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 526—528).—On treating *o*-dibromobenzene with nitric acid of sp. gr. 1.54, adding concentrated nitric acid, and subsequently pouring the product of the reaction into water, a mixture of 3:4-dibromo-1-nitrobenzene and 2:3-dibromo-1-nitrobenzene is obtained. By extracting with 95 per cent. alcohol and cooling the solution, the former is separated and, after a single crystallisation, melts at 57—58°.

Concentration of the alcoholic mother liquors yields a crystalline mixture melting at 42° and, on treating this with acetic acid, 2:3-dibromo-1-nitrobenzene is obtained; it crystallises from acetic acid or ethyl acetate in thick, monoclinic prisms [E. REPOSSI: $a:b:c = 1.031:1.0282$; $\beta = 80^{\circ}8'30''$], melts at 85.2° and dissolves readily in acetone or chloroform, and to a less extent in ether; on replacing the nitro-group by an amino-residue and the latter by a bromine atom, 1:2:3-tribromobenzene, melting at 87.4°, is obtained; when treated with alcoholic ammonia solution at 180°, 2:3-dibromo-1-nitrobenzene yields 2-bromo-6-nitroaniline, which crystallises in pale yellow needles melting at 73.4°, dissolves moderately easily in alcohol, volatilises readily in a current of steam, and is converted by the action of ethyl nitrite into *m*-bromonitrobenzene. When acted on by a mixture of concentrated sulphuric acid and nitric acid of sp. gr. 1.54, 2:3-dibromo-1-nitrobenzene gives a mixture of three dinitro-derivatives.

2:3-Dibromoaniline, prepared by the action of a hydrochloric acid solution of stannous chloride (3 mols.) on 2:3-dibromo-1-nitrobenzene, crystallises from aqueous alcohol in colourless, transparent plates melting at 43°, dissolves readily in alcohol, ether, or ethyl acetate, distils easily in a current of steam, and is a less energetic base than the other *o*-dibromoaniline.

2:3-Dibromoacetanilide, prepared by boiling 2:3-dibromoaniline with acetic anhydride, is slightly soluble in alcohol, from which it separates in acicular crystals melting at 164°.

3-Bromo-2-iodo-1-nitrobenzene, prepared from the bromonitroaniline melting at 73.4° by replacing the amino-group by an iodine atom, forms faintly green, transparent, monoclinic prisms [E. REPOSSI: $a:b:c = 0.634:1:0.568$; $\beta = 74.56^{\circ}$], melting at 119—120°.

2-Chloro-3-bromo-1-nitrobenzene crystallises from alcohol or ether in green, flattened needles melting at 65°. T. H. P.

New Case of Form-analogy and Miscibility of Position-isomeric Benzene Derivatives and the Crystalline Forms of the Six Dibromonitrobenzenes. FRANS M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 26—33).—2:3-Dibromo-1-nitrobenzene crystallises in small, flat, sherry-coloured needles belonging to the triclinic system [$a:b:c = 1.4778:1:1.9513$; $a = 90^{\circ}45\frac{3}{4}'$, $\beta = 110^{\circ}36\frac{3}{4}'$, $\gamma = 89^{\circ}59\frac{1}{4}'$]; the crystals show a decided approach to the monoclinic system. 2:5-Dibromo-1-nitrobenzene forms small, pale yellow, lustrous, flattened, triclinic plates [$a:b:c = 1.4909:1:2.0214$; $a = 90^{\circ}57\frac{1}{2}'$, $\beta = 113^{\circ}21\frac{1}{3}'$, $\gamma = 90^{\circ}2'$]. The two compounds, although closely related, are not isomorphous, but can form an interrupted series of mixed crystals. The binary melting-point curve possesses

a eutectic point at 52° with two per cent. of the compound with higher melting point. The mixed crystals contain up to 48 per cent. of the 1:2:3-derivative and melt between 75° and 84.5° .

The 2:4-dibromo-1-nitrobenzene also crystallises in the triclinic system [$a:b:c=1.1307:1:1.1698$; $\alpha=97^{\circ}36'$, $\beta=113^{\circ}37'$, $\gamma=87^{\circ}33'$], but does not form mixed crystals.

The 2:6:1-, 3:5:1-, and 3:4:1-derivatives belong to the monoclinic system. They do not form mixed crystals in binary mixtures, the lower melting point being lowered on addition of the component melting at the higher temperature. The differences in the crystalline forms of the brominated derivatives are much less than those between the corresponding chlorinated compounds. E. F. A.

Preparation of 1:2-Dichloro-4-nitrobenzene. K. OEHLER (D.R.-P. 167297).—Polyhalogenated nitro-derivatives of aromatic hydrocarbons are generally obtained by nitrating the halogen compounds; the converse operation, the chlorination of the nitro-compound, has not been successfully performed on a technical scale. One part of anhydrous ferric chloride was added to 20 parts of fused *p*-nitrochlorobenzene and chlorine introduced at $95-110^{\circ}$, until the additional weight of the mixture corresponded with 4.5 parts; the mixture was added to water, when a theoretical yield of 1:2-dichloro-4-nitrobenzene was obtained, which, after one crystallisation, gave the correct melting point (43°). The ferric chloride may be replaced by other chlorine carriers, such as iron, phosphorus, antimony pentachloride, or iodine.

G. T. M.

Crystallographic Characters of some Organic Compounds. FRANS M. JAEGER (*Zeit. Kryst. Min.*, 1906, 42, 158—169).—Crystallographic determinations are given of the following compounds: *o*-nitrobenzyl-*o*-toluidine, diphenylhydrazine, 2:4:6-trinitro-*m*-xylene, 4:5:6-trinitro-*m*-xylene, 2:5:6-trinitro-*m*-xylene, 2:3:5-trinitro-*p*-xylene, 1:2-dichloro-3-nitrobenzene, 1:3-dichloro-2-nitrobenzene, 1:3-dichloro-5-nitrobenzene, and 1:4-dichloro-2-nitrobenzene. L. J. S.

Reduction of Aromatic *o*- and *p*-Dinitro-compounds. JAKOB MEISENHEIMER and EGBERT PATZIG (*Ber.*, 1906, 39, 2526—2532. Compare Meisenheimer, *Abstr.*, 1904, i, 150).—The sodium salt, $C_6H_4O_4N_2Na_2$, formed by reduction of *p*-dinitrobenzene by means of hydroxylamine hydrochloride and sodium methoxide in methyl-alcoholic solution, separates almost quantitatively as a red, crystalline powder, detonates slightly when heated, and dissolves and decomposes in aqueous sodium hydroxide.

The volume of nitrogen evolved on reduction of *o*-dinitrobenzene by hydroxylamine in methyl-alcoholic sodium hydroxide solution agrees with that required by the equation $C_6H_4(NO_2)_2 + 2NH_2 \cdot OH + 2KOH = C_6H_4(NO_2K)_2 + 4H_2O + N_2$. The sodium salt, $C_6H_4O_4N_2Na_2$, is obtained as a red, amorphous powder if the reduction takes place in benzene-methyl-alcoholic solution; it dissolves in water or alcohol, forming a dark blue solution, and when treated with bromine in dilute solution at 0° yields *o*-nitronitrosobenzene as a light yellow precipitate. On passage of a current of carbon dioxide, the blue methyl-alcoholic solution of the sodium salt becomes red and sodium hydrogen carbonate

is deposited, the blue solution being again formed on heating. If the solution is diluted with water and saturated with carbon dioxide, *o*-dinitrobenzene is formed slowly.

o-Nitronitroso-*p*-xylene, $C_8H_8O_3N_2$, is prepared by reducing the mixture of *o*- and *m*-dinitro-*p*-xylene obtained by the direct nitration of *p*-xylene (Jannasch and Stuenkel, Abstr., 1881, 808) with hydroxylamine hydrochloride in methyl-alcoholic potassium hydroxide solution, extracting the unchanged *m*-dinitro-compound with ether, and adding hydrochloric acid to the cooled solution; it forms slightly yellow crystals, melts at 130.5° , dissolves in hot benzene, chloroform, or glacial acetic acid to green, in alcoholic alkali hydroxides to red solutions, and does not form a condensation product with aniline in glacial acetic acid solution. G. Y.

Phenylnitrolic Acid. HEINRICH WIELAND and LEOPOLD SEMPER (*Ber.*, 1906, 39, 2522—2526).—*Phenylnitrolic acid*, $NO_2 \cdot CPh \cdot NOH$, is prepared by the successive action of sodium nitrite and oxalic acid on potassium phenylnitromethane in aqueous solution at -15° ; it crystallises from light petroleum in slender, colourless needles, has a bitter flavour, melts at $57-58^\circ$, and decomposes when heated a few degrees above its melting point or more slowly in alkaline solution, forming nitrous acid and benzonitrile oxide (Werner and Buss, Abstr., 1894, i, 585), which rapidly polymerises to diphenylglyoxime peroxide. This crystallises in glistening, colourless leaflets, melts and decomposes at $114-116^\circ$ (105° , Beckmann, Abstr., 1889, 980), and gives Liebermann's nitroso-reaction.

When oxidised carefully with potassium permanganate in alkaline solution, phenylnitrolic acid yields benzenylnitrosolic acid (this vol., i, 412). G. Y.

Behaviour of Sulphonic Acids on Oxidation by Fusion. CARL GRAEBE and HERMANN KRAFT (*Ber.*, 1906, 39, 2507—2512. Compare this vol., i, 255).—When fused with lead peroxide and potassium hydroxide, sulphonic acids are oxidised to the following products, the yields being given in percentages of the theoretical.

p-Toluenesulphonic acid : benzoic acid (78 per cent.) and *p*-hydroxybenzoic acid (2—3 per cent.). *p*-Toluenesulphonamide, 8 per cent. of which remains unchanged : benzoic acid (26.6 per cent.) and *p*-hydroxybenzoic acid (34.7 per cent.). *o*-Toluenesulphonic acid : benzoic acid and *o*-cresol. *o*-Toluenesulphonamide : benzoic acid, *o*-cresol, salicylic acid, and traces of an acid insoluble in chloroform. *o*-Xylene-4-sulphonic acid : phthalic acid (70.5 per cent.). *m*-Xylene-4-sulphonic acid is oxidised only with difficulty : isophthalic acid (33 per cent.) and traces of benzoic and *m*-toluic acids. *p*-Xylenesulphonic acid : terephthalic acid (11 per cent.), *p*-xylenol (26—28 per cent.), and traces of hydroxyterephthalic or salicylic acid. Mesitylenesulphonic acid : trimesic acid (55 per cent.) containing uvitic acid. *p*-Ethylbenzenesulphonic acid : benzoic acid (10 per cent.) and *p*-hydroxybenzoic acid (15 per cent.). *m*-Sulphobenzoic acid : *m*-hydroxybenzoic acid (97 per cent.).

When boiled with aqueous potassium hydroxide and then fused with an anhydrous alkali hydroxide, *o*-tolylsulphone yields benzoic acid (93 per cent.) and a small quantity of an oil having an odour of cresol.

When fused directly with potassium hydroxide, *o*-tolylsulphone is oxidised to benzoic acid and *o*-cresol, the fused mass smelling of benzaldehyde.

When fused with potassium hydroxide, benzaldehyde-4-sulphonic acid yields benzoic (40 per cent.) and *p*-hydroxybenzoic (54 per cent.) acids, benzaldehyde-2-sulphonic acid yields *o*-cresol and benzoic (36.5 per cent.) and salicylic (52 per cent.) acids, whilst *o*-sulphobenzoic acid yields salicylic acid quantitatively. G. Y.

Combination of Mercuric Iodide with Free Amines.

MAURICE FRANCOIS (*J. Pharm. Chim.*, 1906, [vi], 24, 21—24).—A general consideration of facts already recorded (this vol., i, 484). Mercuric iodide combines not only with methylamine (*loc. cit.*), but also with aromatic bases; with aniline the compound $2\text{NH}_2\text{Ph}, \text{HgI}_2$ is obtained, and with pyridine the compound $2\text{C}_5\text{NH}_5, \text{HgI}_2$. The interaction is best effected by warming an alcoholic solution of the base with mercuric iodide; the salt separates in crystals on cooling. The compounds are also formed as a crystalline precipitate by the action of an aqueous solution of the base on a concentrated solution of potassium iodide saturated with mercuric iodide. W. A. D.

Action of Bromine on Aromatic Amines. Substitution Products and Perbromides. KARL FRIES (*Annalen*, 1906, 346, 128—219. Compare Abstr., 1904, i, 571).—On bromination, aromatic amines yield at the ordinary temperature either substitution products or perbromides according to the conditions. The presence of acid is unfavourable to the introduction of bromine into the nucleus. Additive products, perbromides, are produced in the presence of hydrogen halides before substitution takes place, and are converted readily into the substitution products. Perbromides of six types have been observed, X_2Br , XBr , X_2Br_3 , XBr_2 , XBr_4 , and XBr_6 , where X represents the hydrobromide of a base. Hydrochlorides form perbromides of the types XBr and XBr_2 . Hydriodides form perbromides most, and hydrochlorides least, readily. The salts of quaternary bases show the greatest tendency to form perbromides, and the primary amines the least; but the number and nature of the substituting groups exercise a very great influence. The perbromides of unsubstituted bases are very unstable; they can only be obtained by adding bromine at a low temperature to the hydrobromide of the base suspended in hydrobromic acid. Partially substituted amines, on the other hand, yield well-crystallised stable perbromides. The perbromides give up bromine to all substances reacting with bromine, and in the presence of solvents are generally converted into substitution products, when this is possible. Most dry perbromides give up bromine to the air, the higher bromides passing over into the lower perbromides, some of which (those derived from quaternary salts) are stable under these conditions. All perbromides are decomposed by water. When substitution is not possible, oxidation takes place. The perbromides of secondary and tertiary amines lose, with water, an alkyl group, primary or secondary amines being produced. 2:4-Disubstituted tertiary amines behave similarly, but here substitution also takes place, thus: $\text{C}_6\text{H}_3\text{X}_2 \cdot \text{NMe}_2, \text{HBr}, \text{Br}_2 = \text{C}_6\text{H}_2\text{X}_2\text{Br} \cdot \text{NHMe}, \text{HBr} + \text{BrMe}$.

The diperbromide of *p*-bromodimethylaniline hydrobromide behaves in a unique manner; it yields *p*-bromodimethylaniline, 2:4-dibromodimethylaniline, and the perbromide of diphenquinonetetramethyldiiminium dibromide, $\text{Br}_2\cdot\text{NMe}_2\cdot\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot\text{Br}\cdot\text{Br}_2$, which can also be obtained directly by the action of bromine on *p*-bromodimethylaniline.

All the perbromides are similarly constituted, a complex negative ion being present.

The perbromides of all quaternary and many tertiary amines cannot be converted into substitution products, a fact which is in agreement with the direct bromination of aromatic amines. With one mol. of bromine, aniline yields a mixture of mono-, di-, and tri-bromoanilines; methylaniline yields a mixture of mono- and di-bromomethylanilines, and dimethylaniline yields quantitatively bromodimethylaniline. With 2 mols. of bromine, aniline gives the same mixture, monomethylaniline exclusively a dibromo-derivative, and dimethylaniline, dibromodimethylaniline, but with difficulty. Three mols. of bromine convert aniline and methylaniline into the tribromo-derivatives, but transform dimethylaniline into tribromomethylaniline, a methyl group being eliminated. Similar changes are observed if bromine acts on an amine in which a hydrogen atom in the ortho- or the para-positions is already replaced. An alkyl group appears to protect one of the ortho-hydrogen atoms, whilst two alkyl groups prevent both the ortho-hydrogen atoms from being replaced.

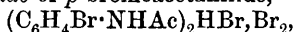
The influence of a bromine atom in the ortho-position relatively to the amino-group on the introduction of alkyl groups has also been investigated. All halogenated amines are less readily alkylated than unsubstituted amines; if the halogen is in the ortho-position with respect to the amino-group, the reaction is still further retarded. Thus, excess of methyl iodide and sodium carbonate alkylated, in thirty hours, 30 per cent. of 2:4-dibromoaniline, 15 per cent. of 3:5-dibromo-*p*-toluidine, and 0 per cent. of *s*-tribromoaniline. Similarly, in the addition of methyl iodide to a tertiary base, it was found that *p*-bromodimethylaniline yielded thirty times as much quaternary iodide as *o*-bromodimethylaniline. Diortho-substituted bases cannot be converted into quaternary bases. It cannot be concluded with certainty that these facts are accounted for by steric hindrance of the reactions.

Large excess of strong acids prevents substitution. Since quaternary salts are also incapable of being substituted, it is argued that the first step in the process of substitution of amines is an addition of the substituting agent to the nitrogen atom.

The *perbromide*, $\text{NH}_2\text{Ph}\cdot\text{HBr}\cdot\text{Br}_2$, is prepared by adding a mixture of bromine and concentrated hydrobromic acid to a mixture of aniline, acetic acid, and hydrobromic acid; it forms yellow crystals, which are reconverted into aniline by treatment with sodium hydrogen sulphite; treated with water or other solvents or on exposure to the air, bromoanilines are formed. *s*-Tribromoaniline yields the *perbromide*, $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{NH}_2\cdot\text{HBr}\cdot\text{Br}_2$, when bromine is added to its solution in acetic acid; it crystallises in garnet-red prisms melting

and decomposing at 105° ; the fused mass resolidifies and again melts at 205° ; all the bromine is eliminated by treatment with solvents or keeping in the air. 3:5-Dibromo-*o*-toluidine gives under the same conditions the *perbromide*, $C_6H_2MeBr_2 \cdot NH_2, HBr, Br_2$, which forms dark red prisms, losing bromine at 120° and melting at 240° . The corresponding *derivative* of dibromo-*p*-toluidine crystallises in brownish-red plates, which lose bromine at 110° and melt at 225° . *Diacetyl-5-bromo-1:3:4-xylylidine*, prepared by prolonged boiling of 5-bromo-*m*-xylylidine with acetic anhydride, crystallises in prisms melting at 59° . 6-Bromo-1:3:4-xylylidine is the chief product of the bromination of *m*-xylylidine in concentrated sulphuric acid; its *diacetyl* derivative crystallises in plates melting at 70° . 5:6-Dibromo-1:3:4-xylylidine, $C_6HMe_2Br_2 \cdot NH_2$, is better prepared from 6-bromo- than from 5-bromo-*m*-xylylidine; it crystallises in needles melting at 40° . Its *monoacetyl* derivative crystallises in needles melting at 192° , and its *diacetyl* derivative in prisms melting at 183° . *m*-Xylylidine in hydrobromic acid yields the *perbromide*, $C_6H_3Me_2 \cdot NH_2, HBr, Br_2$ (?), which appears to be identical with the compound mistaken by Fischer and Windaus (Abstr., 1900, i, 484) for a bromoamine; it crystallises in yellow needles, which readily lose bromine, and is converted by contact with solvents into bromoxylylidine. The *perbromide*, $C_6H_2Me_2Br \cdot NH_2, HBr, Br_2$, obtained from 5-bromoxylylidine, crystallises in plates melting at 134° .

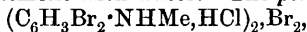
When acetanilide is treated with 1 mol. of bromine in glacial acetic acid, a *perbromide* of *p*-bromoacetanilide,



is obtained as yellow plates melting at 135° ; on addition of water during the bromination the *perbromide* is decomposed, *p*-bromoacetanilide alone being formed. In order to form 2:4-dibromoacetanilide, dilute acetic acid should be used and sodium acetate added. *s*-Tribromoacetanilide can only be obtained in a yield of 15 per cent. when acetanilide is brominated.

When 1:3:4-acetxylylidide is brominated, besides the 6-bromo-derivative both the 5- and the 2-bromo-derivatives are produced.

2:4-Dibromomethylaniline, $C_6H_3Br_2 \cdot NHMe$, prepared by brominating methylaniline in acetic acid and then cautiously adding water, crystallises in leaflets melting at 48° . 2:4:6-Tribromomethylaniline, prepared similarly, crystallises in needles melting at 39° , boils at 310° , and forms a very sparingly soluble hydrochloride and hydrobromide; the *platinichloride* crystallises in orange plates decomposing at 232° , and the *acetyl* derivative in plates melting at 101° . The *perbromide* of dibromomethylaniline, $(C_6H_3Br_2 \cdot NHMe, HBr)_2, Br_2$, is prepared either from dibromomethylaniline or from bromomethylaniline in the presence of hydrobromic acid, and crystallises in yellowish-red prisms melting at 125° ; it is converted into tribromomethylaniline by treatment with water. The *perbromide*,



crystallises in prisms, becoming colourless at 100° and melting at 190° . The *perbromide* from tribromomethylaniline, $C_6H_2Br_3 \cdot NHMe, HBr, Br_2$, crystallises in brownish-red needles melting at about 160° ; addition of water to its solution in acetic acid converts it into tribromoaniline. The *perbromide*, $C_6H_2Br_3 \cdot NHMe, HCl, Br_2$, forms yellowish-red plates

which melt at 150° and change in the air into the hydrochloride of *s*-tribromomethylaniline, which crystallises in prisms decomposing at 190° ; water converts this perbromide into *s*-tribromoaniline.

5-Bromomethyl-o-toluidine, $C_6H_3MeBr \cdot NHMe$, prepared from methyl-*o*-toluidine, is an oil boiling at 165° under 25 mm. pressure; the corresponding 3:5-dibromo-compound boils at 187° under 50 mm. pressure, and yields a *hydrobromide* which darkens at 180° and melts at 220° . The *perbromide*, $C_6H_3MeBr \cdot NHMe, HBr, Br_2$, prepared directly from methyl-*o*-toluidine, crystallises in red prisms decomposing at 105° , and is converted by warming with solvents into dibromo-*o*-toluidine. The *perbromide*, $C_6H_2MeBr_2 \cdot NHMe, HBr, Br_2$, obtained from 3:5-dibromomethyltoluidine, crystallises in prisms melting at 142° and is converted by water into 3:5-dibromo-*o*-toluidine.

p-Bromoethylaniline, $C_6H_4Br \cdot NHEt$, prepared from ethylaniline, melts at 12° ; 2:4-dibromoethylaniline crystallises in plates melting at 51° ; 2:4:6-tribromoethylaniline, prepared directly from ethylaniline, crystallises in needles melting at 45° . The *perbromide*, $C_6H_3Br_2 \cdot NHEt, HBr, Br_2$, prepared from 2:4-dibromoethylaniline in the presence of hydrobromic acid, crystallises in yellowish-red plates melting at 85° , and when warmed with acetic acid passes into tribromoethylaniline. The *perbromide*, $C_6H_2Br_3 \cdot NHEt, HBr, Br_2$, crystallises in yellowish-brown prisms melting at 125° , and when heated with dilute acetic acid is converted into tribromoaniline.

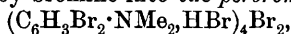
3-Bromoethyl-*p*-toluidine, $C_6H_3MeBr \cdot NHEt$, is an oil boiling at 143° under 25 mm. pressure; its *hydrobromide* crystallises in prisms decomposing at about 160° . 3:5-Dibromoethyl-*p*-toluidine is an oil boiling at 169° under 20 mm. pressure; its *hydrobromide* crystallises in needles melting at 185° . The *perbromide*,

$C_6H_2MeBr_2 \cdot NHEt, HBr, Br_2$,
crystallises in golden-yellow needles melting at 110° , and is converted into 3:5-dibromo-*p*-toluidine by warming with water.

p-Bromodimethylaniline is formed easily from dimethylaniline and bromine in acetic acid solution; its *hydrobromide* crystallises in prisms melting at 105° and decomposing at 185° , and the *hydriodide* forms crystals melting at 145° . 2:4-Dibromodimethylaniline,

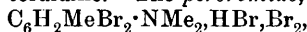
$C_6H_3Br_2 \cdot NMe_2$,
is prepared by treating dimethylaniline with excess of bromine in acetic acid solution and then decomposing the perbromide thus formed with sodium acetate, or directly by methylating dibromoaniline or dibromomethylaniline; it is an oil boiling at 275° under 740 mm. pressure; its *stannochloride* crystallises in plates decomposing at 240° , and its *platinichloride* in golden-yellow needles melting at 237° ; the *hydrobromide* crystallises in prisms. 2:4:6-Tribromodimethylaniline, prepared by methylating tribromomethylaniline with methyl sulphate and magnesium oxide, is an oil boiling at 301° under 750 mm. pressure; it reacts with bromine, giving tribromomethylaniline, but not with methyl iodide or methyl sulphate; the *platinichloride* crystallises in prisms sintering at 180° and melting at 190° . The *perbromide* from dimethylaniline, $NPhMe_2, HBr, Br_2$, forms reddish-brown crystals which are easily reduced to dimethylaniline and are readily converted into *p*-bromodimethylaniline. The *perbromide*,

$(C_6H_4Br \cdot NMe_2, HBr)_2Br_2$, is prepared directly from dimethylaniline in acetic acid solution, and forms dark red crystals, sintering at 95° and melting at 107° . The *perbromide*, $C_6H_4Br \cdot NMe_2, HBr, Br_2$, is formed when 1 mol. of dimethylaniline and 2 mols. of bromine are used; it crystallises in dark red plates sintering at 75° and melting at 85° ; on keeping in the air it passes over into the *perbromide* last mentioned. With water it yields the dibromodimethylaniline and the *perbromide* of diphenoquinonetetramethyldi-iminium dibromide; the latter is also formed from bromine and tetramethylbenzidine; it is a brownish-red powder melting at about 158° , is reduced to tetramethylbenzidine, and is coloured bluish-green by alkali hydroxides. Tetramethylbenzidine also gives with bromine a dark green, amorphous compound, $C_{16}H_{20}N_2Br_2$, which sinters at 70° and melts at 90° , and is reduced to tetramethylbenzidine; concentrated sulphuric or hydrochloric acids give red, crystalline products, and bromine converts it into the *perbromide* last mentioned. Dibromodimethylaniline hydrobromide is converted by bromine into the *perbromide*,



which crystallises in green plates melting at 135° . The same salt also yields the *perbromide*, $C_6H_3Br_2 \cdot NMe_2, HBr, Br_2$, which crystallises in prisms melting at 102° . The *perbromide*, $C_6H_2Br_3 \cdot NMe_2, HBr, Br_2$, prepared from tribromodimethylaniline, crystallises in pale yellowish-red needles melting at 124° , and is converted by water into tribromomethylaniline.

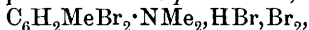
5-Bromodimethyl-*o*-toluidine, $C_6H_3MeBr \cdot NMe_2$, boils at 246° , its *platinichloride* crystallises in golden-yellow prisms decomposing at 240° . 3:5-Dibromodimethyl-*o*-toluidine, prepared by alkylating dibromotoluidine, is an oil boiling at 277° under 751 mm. pressure; it does not react either with methyl iodide or methyl sulphate, and when treated with bromine in acetic acid solution yields *dibromomethyltoluidine*, a methyl group being eliminated; the last-mentioned base is also directly produced by the action of bromine on dimethyl-*o*-toluidine, and decomposing the *perbromide* first formed with sodium acetate; it is an oil boiling at $185-187^\circ$ under 50 mm. pressure, and forms a *hydrobromide* which crystallises in plates decomposing at 220° . Dimethyl-*o*-toluidine forms the *perbromide*, $C_6H_4Me \cdot NMe_2, HBr, Br_2$, which crystallises in needles or plates melting at 68° , and is converted by treatment with solvents into 5-bromodimethyl-*o*-toluidine. The *perbromide*, $(C_6H_3MeBr \cdot NMe_2, HBr)_2Br_2$, prepared from 1 mol. of dimethyl-*o*-toluidine and $1\frac{1}{2}$ mols. of bromine, crystallises in dark red needles and is converted by water into a mixture of bromodimethyl- and dibromomethyl-*o*-toluidine. The *perbromide*,



obtained from dimethyl-*o*-toluidine and 2 mols. of bromine, crystallises in plates or prisms melting at 85° and decomposing at 140° . The *perbromide*, $C_6H_2MeBr_2 \cdot NMe_2, HBr, Br_2$, crystallises in yellowish-red needles melting at 112° , and is converted by water into dibromomethyltoluidine.

3-Bromodimethyl-*p*-toluidine, prepared by brominating dimethyl-*p*-toluidine, is an oil boiling at 239° under 750 mm. pressure, and is converted by bromine into the 3:5-dibromomonomethyl-*p*-toluidine, which

boils at 154° under 16 mm. pressure. 3:5-Dibromodimethyl-*p*-toluidine, prepared by methylating the dibromotoluidine, is an oil boiling at 270° under 750 mm. pressure. The *perbromide*,



crystallises in prisms melting at 130° , and on treatment with water loses methyl bromide.

2:4-Dibromodiethylaniline, $\text{C}_6\text{H}_3\text{Br}_2 \cdot \text{NEt}_2$, formed on treating with sodium acetate the *perbromide* produced by the action of bromine on diethylaniline, is an oil boiling at 285° under 751 mm. pressure; it is converted by further treatment with bromine into *s*-tribromoaniline; its *platinichloride* crystallises in yellowish-red prisms melting at 207° , and its *stannochloride* forms crystals melting at 235° . The *perbromide*, $\text{NPhEt}_2, \text{HBr}, \text{Br}_2$, is a red oil, which is converted by water into *p*-bromodiethylaniline. The *perbromide*, $(\text{C}_6\text{H}_4\text{Br} \cdot \text{NEt}_2, \text{HBr})_2\text{Br}_2$, crystallises in prisms melting at 75° , and is converted by water into 2:4-dibromodiethylaniline and a quinonoid derivative of tetraethylbenzidine. Diethylaniline also yields the *perbromide*, $(\text{C}_6\text{H}_4\text{Br} \cdot \text{NEt}_2, \text{HBr})_4\text{Br}_6$, which crystallises in red prisms melting at 81° .

4:4'-Dibromodiphenylmethylamine, $\text{C}_{13}\text{H}_{11}\text{NBr}_2$, prepared from diphenylmethylamine and bromine, crystallises in needles melting at 120° . 2:2':4:4'-Tetrabromodiphenylmethylamine, $\text{C}_{13}\text{H}_9\text{NBr}_4$, prepared by warming the *perbromide* formed from diphenylmethylamine with the solvent, crystallises in prisms melting at 142° ; bromine converts it into tetrabromodiphenylamine. Dibromodiphenylmethylamine yields a *perbromide*, $(\text{C}_6\text{H}_4\text{Br})_2\text{NMe}, \text{HBr}, \text{Br}_2$ (?), which forms red crystals, and is transformed by solvents into a mixture of tetrabromodiphenylmethylamine and tetrabromodiphenylamine.

The *perbromide*, $\text{NPhMe}_3\text{Br}, \text{Br}_4$, prepared from phenyltrimethylammonium bromide, crystallises in bluish-red prisms melting at 40° , and is converted into the dibromide on exposure to the air. *p*-Tolyltrimethylammonium bromide crystallises in prisms melting at 219° , and is converted by bromine into the *perbromide*, $\text{C}_6\text{H}_4\text{Me} \cdot \text{NMe}_3\text{Br}, \text{Br}_2$, which forms yellow, four-sided plates melting at 113° , from which, by further treatment with bromine, the *perbromide*,



is obtained; it forms dark red crystals melting at 45° . K. J. P. O.

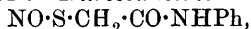
Crystalline Forms of the 2:4-Dinitroaniline Derivatives Substituted in the NH_2 -Group. FRANS M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 23—25).—The melting points, molecular weights, equivalent volumes in the solid state, symmetry, axial elements, and topic parameters of 31 derivatives of 2:4-dinitroaniline are recorded in tabular form. The substances all have the same family character, only a few showing no simple relationship to the rest. E. F. A.

Nitration of Acetanilide. ARNOLD F. HOLLEMAN and C. H. SLUITER (*Rec. trav. chim.*, 1906, 25, 208—212).—The authors have examined the products of the nitration of acetanilide in order to determine if the quantity of the secondary products is affected by the concentration of the nitric acid employed (compare Körner, this Journal, 1876, i, 204);

the results show that when acetanilide is slowly added to ten times its weight of nitric acid of sp. gr. 1.46 at 0°, the product is pure *p*-nitroacetanilide; if nitric acid of a higher specific gravity is employed, 2:4-dinitroacetanilide is formed as a secondary product, the quantity increasing with the increase in the concentration of the nitric acid, but no *o*-nitroacetanilide is produced (compare Körner, *loc. cit.*; Beilstein and Kurbatoff, *Annalen*, 1879, 197, 83); if, however, acetanilide is added rapidly to nitric acid of sp. gr. 1.52, a small quantity of *o*-nitroacetanilide is formed owing to the increase in temperature caused by the more violent reaction. M. A. W.

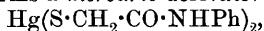
Thio-fatty Anilides. HEINRICH BECKURTS and GUSTAV FRERICHS (*J. pr. Chem.*, 1906, [ii], 74, 25—50. Compare Abstr., 1902, i, 763). —[With L. HARTWIG.]—*Methylthiolacetanilide*, $\text{SMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$, prepared by the action of methyl iodide and alcoholic potassium hydroxide on thioglycollanilide in a sealed tube in the water-bath, crystallises in colourless leaflets, melts at 74°, and is readily soluble in alcohol or ether. *n-Propylthiolacetanilide*, $\text{SPr}^{\alpha}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$, crystallises in colourless needles and melts at 57°. *iso-Propylthiolacetanilide*, $\text{SPr}^{\beta}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$, forms flat needles and melts at 67°. *Ethylenedithiolodiacetanilide*, $\text{C}_2\text{H}_4(\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh})_2$, crystallises in colourless needles, melts at 158°, and is only sparingly soluble in cold alcohol. *Propylenedithiolodiacetanilide*, $\text{C}_3\text{H}_6(\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh})_2$, forms colourless needles and melts at 154—155°. *Carboxymethylthiolacetanilide*, $\text{CO}_2\text{Me}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$, formed from methyl chlorocarbonate and thioglycollanilide, crystallises in colourless needles, melts at 83°, and is readily soluble in alcohol. *Benzylthiolacetanilide*,
 $\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$,

forms colourless, flat needles, melts at 73.5°, and is readily soluble in alcohol. *Benzylidenedithiolodiacetanilide*, $\text{CHPh}(\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh})_2$, formed by the action of benzaldehyde or of benzylidene dichloride and potassium hydroxide on thioglycollanilide, crystallises in colourless needles and melts at 182°. *Nitrosothiolacetanilide*,



formed by the action of potassium nitrite and hydrochloric acid on thioglycollanilide in aqueous solution, crystallises in red needles, decomposes when heated, yielding nitric oxide and dithioglycollanilide, and is readily soluble in alcohol or ether.

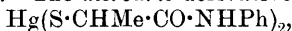
Thioglycollanilide forms a *mercuric* derivative,



which crystallises in glistening leaflets and decomposes when heated, and a *mercurichloride*, $\text{HgCl}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$, which is obtained as a yellowish-white, crystalline powder, insoluble in the ordinary solvents.

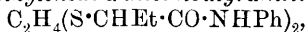
α-Methylthiolpropanilide, $\text{SMe}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NHPh}$, formed by the action of methyl iodide and potassium hydroxide on *α*-thiolpropanilide in alcoholic solution, crystallises in glistening, colourless needles and melts at 126°. *α-n-Propylthiolpropanilide*, $\text{SPr}^{\alpha}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NHPh}$, crystallises in needles and melts at 92°. *α-iso-Propylthiolpropanilide*, $\text{C}_{12}\text{H}_{17}\text{ONS}$, forms colourless needles melting at 84°. *Ethylenedi-α-thiolpropylpropanilide*, $\text{C}_2\text{H}_4(\text{S}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NHPh})_2$, crystallises in colourless needles melting at 172—174°. *Propylenedi-α-thiolpropylpropanilide*,

$C_3H_6(S \cdot CHMe \cdot CO \cdot NHPh)_2$, forms a slightly yellow, viscid oil. *α*-Carboxymethylthiolpropanilide, $CO_2Me \cdot S \cdot CHMe \cdot CO \cdot NHPh$, crystallises in glistening leaflets and melts at 103.5° . *α*-Benzylthiolpropanilide, $CH_2Ph \cdot S \cdot CHMe \cdot CO \cdot NHPh$, crystallises in colourless, flat needles and melts at 119.5° . *Benzylidenedi-α-thioldipropanilide*, $CHPh(S \cdot CHMe \cdot CO \cdot NHPh)_2$, forms colourless needles and melts at 187° . *α-Nitrosothiolpropanilide*, $NO \cdot S \cdot CHMe \cdot CO \cdot NHPh$, is obtained as an unstable red oil. The mercuric derivative,



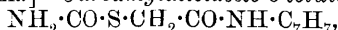
separates from glacial acetic acid in small crystals and melts and decomposes above 200° . The mercurichloride, $HgCl \cdot S \cdot CHMe \cdot CO \cdot NHPh$, forms a crystalline powder and melts and decomposes at $110-120^\circ$.

α-Methylthiolbutyranilide, $SMe \cdot CHEt \cdot CO \cdot NHPh$, crystallises in colourless needles and melts at $111-112^\circ$. *α-isoPropylthiolbutyranilide*, $SPr^i \cdot CHEt \cdot CO \cdot NHPh$, forms colourless, flat needles and melts at $87-88^\circ$. *Ethylenedi-α-thioldibutyranilide*,



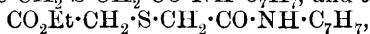
forms colourless crystals melting at 125° . *Propylenedi-α-thioldibutyranilide*, $C_3H_6(S \cdot CHEt \cdot CO \cdot NHPh)_2$, is obtained as a viscid, yellow oil which gradually crystallises. *α*-Carboxymethylthiolbutyranilide, $CO_2Me \cdot S \cdot CHEt \cdot CO \cdot NHPh$, forms colourless needles melting at 82° . *α*-Benzylthiolbutyranilide, $CH_2Ph \cdot S \cdot CHEt \cdot CO \cdot NHPh$, crystallises in colourless needles melting at 89° . *Benzylidenedi-α-thioldibutyranilide*, $CHPh(S \cdot CHEt \cdot CO \cdot NHPh)_2$, forms colourless leaflets melting at 148° . *α-Nitrosothiolbutyranilide*, $NO \cdot S \cdot CHEt \cdot CO \cdot NHPh$, is obtained as an unstable red oil. The mercuric derivative, $Hg(S \cdot CHEt \cdot CO \cdot NHPh)_2$, and the mercurichloride, $HgCl \cdot S \cdot CHEt \cdot CO \cdot NHPh$, form micro-crystalline powders which decompose when heated.

[With CARL BEYER.]—*Carbamylthiolaceto-o-toluidide*,

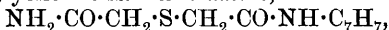


prepared by heating chloroacetic acid and *o*-toluidine with potassium thiocyanate in aqueous solution, crystallises in colourless needles, melts at $123-124^\circ$, and when dissolved in hot 10 per cent. ammonia and precipitated by hydrochloric acid in an atmosphere of carbon dioxide yields *thiolaceto-o-toluidide*, $SH \cdot CH_2 \cdot CO \cdot NH \cdot C_7H_7$, which crystallises in colourless needles, melts at $84-85^\circ$, and is readily soluble in alcohol. *Dithiodiaceto-o-toluidide*, $S_2(CH_2 \cdot CO \cdot NH \cdot C_7H_7)_2$, crystallises in colourless needles melting at $164-165^\circ$. The following derivatives of *thiolaceto-o-toluidide*, in which $R = S \cdot CH_2 \cdot CO \cdot NH \cdot C_7H_7$, have been prepared; the temperatures given are melting points: *methyl*, $Me \cdot R$: colourless leaflets, $65-66^\circ$; *ethyl*, $Et \cdot R$: colourless needles, $60-61^\circ$; *ethylenedi*, $C_2H_4R_2$: colourless nodules, $184-185^\circ$; *dimethylmethylenedi*, CM_2R_2 : colourless leaflets, $160-161^\circ$; *n-propyl*, $Pr^a \cdot R$, colourless needles, $57-58^\circ$; *isopropyl*, $CHMe_2R$: colourless needles, $61-62^\circ$; *benzyl*, $CH_2Ph \cdot R$: colourless needles, $74-75^\circ$; *carboxymethyl*, $CO_2Me \cdot R$: colourless needles, $90-91^\circ$; *carboxyethyl*, $CO_2Et \cdot R$: colourless needles, $78-79^\circ$.

Thioldiaceto-o-toluidamic acid, $CO_2H \cdot CH_2 \cdot S \cdot CH_2 \cdot CO \cdot NH \cdot C_7H_7$, formed from chloroacetic acid and *thiolaceto-o-toluidide*, crystallises in colourless nodules, melts at $125-126^\circ$, and is readily soluble in alcohol. The *methyl*, $CO_2Me \cdot CH_2 \cdot S \cdot CH_2 \cdot CO \cdot NH \cdot C_7H_7$, and *ethyl*,

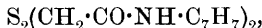


esters form viscid, yellow oils. The *amide*,



forms colourless needles and melts at 150—151°. Thioldiacetodi-*o*-toluidide, formed from thiolaceto-*o*-toluidide and chloroacetyl-*o*-toluidide, is identical with Grothe's product from chloroacetyl-*o*-toluidide and potassium hydrogen sulphide (Abstr., 1901, i, 79).

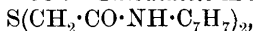
Thiolaceto-m-toluidide, $\text{SH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$, crystallises in colourless needles and melts at 152—153°. *Dithiodiaceto-m-toluidide*,



forms colourless needles and melts at 162—163°. The following derivatives of thiolaceto-*m*-toluidide, in which $\text{R} = \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$, are described; the temperatures given are melting points:

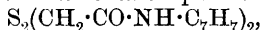
Carbamyl-, $\text{NH}_2 \cdot \text{CO} \cdot \text{R}$: colourless needles, 151—152°; *methyl-*, $\text{Me} \cdot \text{R}$: colourless needles, 52—53°; *ethyl-*, $\text{Et} \cdot \text{R}$: a yellow oil; *ethylenedi-*, $\text{C}_2\text{H}_4\text{R}_2$: colourless needles, 127—128°; *hydroxyethyl-*, $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{R}$: colourless needles, 89—90°; *dimethylmethylenedi-*, CMe_2R_2 : colourless leaflets, 141—142°; *benzyl-*, $\text{CH}_2\text{Ph} \cdot \text{R}$: colourless needles, 39—40°, *carboxymethyl-*, $\text{CO}_2\text{Me} \cdot \text{R}$: a viscid oil; *carboxyethyl-*, $\text{CO}_2\text{Et} \cdot \text{R}$: colourless leaflets, 82—83°.

Thiodiaceto-m-toluidamic acid, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$, forms colourless leaflets melting at 99—100°. The *methyl*, $\text{C}_{12}\text{H}_{15}\text{O}_3\text{NS}$, and *ethyl*, $\text{C}_{13}\text{H}_{17}\text{O}_3\text{NS}$, esters are obtained as viscid, yellow oils. The *amide*, $\text{NH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$, crystallises in colourless nodules and melts at 97—98°. *Thiodiaceto-m-toluidide*,



crystallises in colourless needles and melts at 135—136°.

Thiolaceto-p-toluidide, $\text{C}_9\text{H}_{11}\text{ONS}$, crystallises in colourless needles and melts at 125—126°. *Dithiodiaceto-p-toluidide*,



crystallises in colourless needles and melts at 180—182°. The following derivatives of thiolaceto-*p*-toluidide, $\text{R} = \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$, are described; the temperatures given are melting points:

Carbamyl-, $\text{NH}_2 \cdot \text{CO} \cdot \text{R}$: colourless leaflets, 196°; *methyl-*, $\text{Me} \cdot \text{R}$: colourless needles, 102—103°; *ethyl-*, $\text{Et} \cdot \text{R}$: colourless needles, 84—85°; *ethylenedi-*, $\text{C}_2\text{H}_4\text{R}_2$: colourless needles, 194—195°; *hydroxyethyl-*, $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{R}$: colourless needles, 87—88°; *dimethylmethylenedi-*, CMe_2R_2 : colourless needles, 182—183°; *n-propyl-*, $\text{Pr}^\alpha \cdot \text{R}$: colourless needles, 80—81°; *isopropyl-*, $\text{Pr}^\beta \cdot \text{R}$: colourless needles, 66—67°; *benzyl-*, $\text{CH}_2\text{Ph} \cdot \text{R}$: colourless needles, 73—74°; *benzylidenedi-*, CHPhR_2 : colourless needles, 185—186°; *carboxymethyl-*, $\text{CO}_2\text{Me} \cdot \text{R}$: 96—97°; *carboxyethyl-*, $\text{CO}_2\text{Et} \cdot \text{R}$: colourless needles, 126—127°.

Thiodiaceto-p-toluidamic acid, $\text{C}_{11}\text{H}_{13}\text{O}_3\text{NS}$, forms colourless crystals and melts at 101—102°. The *methyl* ester, $\text{C}_{12}\text{H}_{15}\text{O}_3\text{NS}$, melts at 38—39°; the *ethyl* ester, $\text{C}_{13}\text{H}_{17}\text{O}_3\text{NS}$, melts at 46—47°; the *amide*, $\text{NH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$, crystallises in colourless leaflets and melts at 148—149°.

G. Y.

Direct Introduction of Amino-groups into the Nucleus of Aromatic Nitro-compounds. JAKOB MEISENHEIMER and EGBERT PATZIG (*Ber.*, 1906, 39, 2533—2542).—The action of hydroxylamine

hydrochloride on *m*-dinitrobenzene in alcoholic sodium ethoxide solution leads to the formation of a light red *sodium* salt, $C_6H_3O_6N_4Na_2$, which detonates slightly when heated or on contact with a small quantity of water, is more stable in the presence of an alkali hydroxide, and on acidification yields *m*-dinitrobenzene. The cooled aqueous solution of the sodium salt gradually deposits *m*-dinitro-*m*-phenylenediamine, whilst the diluted aqueous-alcoholic solution yields *m*-dinitro-*m*-phenylenediamine, *m*-dinitrobenzene, and 2:4-dinitroaniline, which is converted into *m*-dinitro-*m*-phenylenediamine by the further action of hydroxylamine.

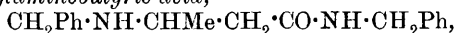
The *sodium* salt, $C_7H_{11}O_9N_6Na_3 \cdot 3H_2O$, obtained in the same manner from *s*-trinitrobenzene as an intensely red, granular precipitate, gradually decomposes in a vacuum, forming ammonia, detonates when heated, and yields picramide and *s*-trinitro-*m*-phenylenediamine on addition of an acid to its aqueous solution at 0° .

2:6-Dinitro-3-toluidine, $C_7H_7O_4N_3$, is obtained in a 10–15 per cent. yield by the action of hydroxylamine hydrochloride on 2:6-dinitro-toluene in methyl-alcoholic potassium hydroxide solution at 30° and addition of much water to the resulting solution; it forms glistening, yellow crystals, melts at 132.5° , and is readily soluble in alcohol.

2-Nitro- α -naphthylamine is formed in the same manner from β -nitronaphthalene; if the product is allowed to remain in contact with the reaction solution, it is converted slowly into 2-nitro- α -naphthol.

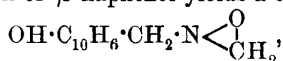
The action of hydroxylamine on ethyl *m*-nitrobenzoate in concentrated, alkaline, absolute alcoholic solution leads to the formation of the *sodium* salt of *m*-nitrobenzhydroxamic acid, $C_7H_5O_4N_2Na$; the acid melts at 153° (m. p. 151° : Werner and Skiba, Abstr., 1899, i, 690). *m*-Nitrobenzaldehyde and hydroxylamine react in alkaline solution, forming *m*-nitrobenzaldoxime melting at 123° (121° : Ciamician and Silber, Abstr., 1904, i, 161; 119° : Gabriel, Abstr., 1883, G. Y., 581, 919).

Action of Benzylamine on Ethyl α -Crotonate. GIOVANNI SANI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 645–646).—The *benzylamide* of *benzylaminobutyric acid*,



prepared by heating ethyl α -crotonate (1 mol.) and benzylamine (2 mols.) with absolute alcohol in a sealed tube at 150° , separates from ether in shining, well-developed, rhombic crystals [ARTINI: $a:b:c = 1.1113:1.04774$], melts at 115 – 116° , and is soluble in alcohol. T. H. P.

Reaction between β -Naphthol, Formaldehyde, and Hydroxylamine. MARIO BETTI (*Gazzetta*, 1906, 36, i, 388–401. Compare Abstr., 1904, i, 581).—The action of formaldehyde and hydroxylamine on an alcoholic solution of β -naphthol yields a *compound*,



which crystallises from alcohol in mammillary masses of slender, white needles, melting and decomposing at 149° , and dissolves in benzene,

chloroform, or dilute sodium hydroxide solution, and sparingly in light petroleum; the cold alcoholic solution gives an intense reddish-brown coloration with aqueous ferric chloride. If the reaction proceeds in neutral or alkaline solution, the above compound is accompanied by methylenedinaphthol.

In alcoholic solution, the compound melting at 149° is transformed, slowly in the cold and more rapidly on boiling, into *di-β-naphtholmethylenedihydroxylamine*, $\text{OH}\cdot\text{N}(\text{CH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH})_2$, which crystallises from alcohol in shining, straw-yellow rhombohedra melting and decomposing at 227° , and dissolves sparingly in all organic solvents. On boiling with 20 per cent. hydrochloric acid, the compound melting at 149° is converted into *di-β-naphtholmethylenedihydroxylamine hydrochloride*, $\text{C}_{22}\text{H}_{19}\text{O}_3\text{N}\cdot\text{HCl}$, which forms a crystalline powder with an ill-defined melting point above 200° .

By treating with sodium hydroxide solution and subsequently saturating the liquid with carbon dioxide, the compound is converted into methylenedi-β-naphthol and di-β-naphtholmethylenedihydroxylamine.

The *acetyl* derivative, $\text{OAc}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\cdot\text{N}<\overset{\text{O}}{\underset{\text{CH}_2}{\text{C}}}$, crystallises from alcohol in shining prisms melting at 130° , and exhibits normal cryoscopic behaviour in acetic acid solution.

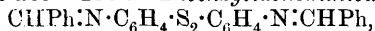
Dibenzoyl-β-naphtholmethylenedihydroxylamine, $\text{OBz}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\cdot\text{NBz}\cdot\text{OH}$, prepared by the action of benzoyl chloride on the compound melting at 149° , dissolved in sodium hydroxide solution, separates from a mixture of alcohol and benzene in highly refractive, shining rhombohedra melting at 177° .

β-Naphtholmethylenamine, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\cdot\text{NH}_2$, obtained by reducing the crude compound melting at 149° by means of zinc dust and hydrochloric acid, crystallises from light petroleum in colourless needles melting at 115 – 116° and reddens and oxidises slowly in the air, and more rapidly in a faintly alkaline solution. The *hydrochloride*, $\text{C}_{11}\text{H}_{11}\text{ON}\cdot\text{HCl}$, crystallises from a mixture of alcohol and hydrochloric acid in white needles melting and decomposing at 226 – 227° .

Di-β-naphtholmethylenamine, $\text{NH}(\text{CH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH})_2$, also obtained by reducing the crude compound melting at 149° , crystallises from aqueous alcohol in white, prismatic needles melting at 163° . The *hydrochloride*, $\text{C}_{22}\text{H}_{19}\text{O}_2\text{N}\cdot\text{HCl}$, separates from alcohol, acidified with hydrochloric acid, in colourless, rhombohedral crystals melting and decomposing at 220° .

T. H. P.

Isomerism of *ar*-Thio-compounds. OSCAR HINSBERG (*Ber.*, 1906, 39, 2427–2436. Compare *Abstr.*, 1905, i, 518).—The dithioaniline melting at 76 – 77° is now found to be identical with Schmidt's 4 : 4'-dithioaniline melting at 78 – 79° (m. p. 80° ; Hofmann, *Abstr.*, 1895, i, 132). It forms two acetyl derivatives: that melting at 182° is labile, and changes slowly at the ordinary temperature into the stable acetate melting at 215 – 216° . *Dibenzylidenedithioaniline*,



is obtained in only one modification, which crystallises from alcohol in yellow needles, melts at 136° , and yields benzaldehyde when treated with dilute mineral acids.

The reduction of 4 : 4'-dithioaniline with zinc dust and hydrochloric acid leads to the formation of a solution containing *p*-aminophenyl mercaptan, which is oxidised on exposure to air, forming 4 : 4'-dithioaniline, and, on addition of acetic acid, separates as an oil; this has an unpleasant odour and is soluble in mineral acids or aqueous alkali hydroxides.

p-Acetylaminophenyl mercaptan, $\text{SH} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}$ (Hofmann, Abstr., 1894, i, 87), is obtained on boiling 4 : 4'-dithioacetanilide with aluminium powder and acetic acid as a mixture of two modifications, crystallising in small, yellow leaflets. The colourless form obtained on adding hydrochloric acid to a cold alkaline solution of the mixture crystallises in white scales, commences to sinter at about 145° , melts at 154° , has in aqueous solution a slight mercaptan odour, and reddens litmus. With lead acetate, it gives a chocolate-brown, with silver nitrate a yellow precipitate, and is oxidised by air to 4 : 4'-dithioacetanilide melting at 215 – 216° , or by ferric chloride and a small quantity of hydrochloric acid to a mixture of the two isomerides melting at 160 – 215° . The yellow modification of *p*-acetylaminophenyl mercaptan is obtained on cooling the hot saturated aqueous solution of the mixture to 70° ; it forms yellowish-red leaflets or flat prisms and melts at 154° . Dilute solutions or concentrated solutions below 70° deposit the colourless modification. The conversion of the colourless into the yellow form takes place also slowly at 100 – 137° on exposure to sunlight, or quickly on crystallisation from methyl or ethyl alcohol.

p-Acetylaminophenyl methyl thioether, $\text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}$, is formed by treating the lead or silver salt with methyl iodide at the ordinary temperature, by heating the mercaptan with methyl iodide and sodium hydroxide in alcohol solution, by heating the sodium mercaptide with potassium methyl sulphate and methyl alcohol at 170° , or by the action of methyl iodide on the mercaptan in pyridine solution. It crystallises in colourless leaflets or thin needles, melts at 128° , and is readily soluble in alcohol, ether, or glacial acetic acid.

Diacetyl-p-aminophenyl mercaptan, $\text{SAC} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}$, formed by the action of acetic anhydride on the aminomercaptan in aqueous sodium hydroxide solution, crystallises in colourless leaflets and melts at 144° .

Dithiobenzanilide, $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{S}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NHBz}$, formed by heating dithioaniline with benzoic anhydride, is obtained as a colourless, crystalline powder melting at 264° . When heated with aluminium powder, glacial acetic acid, and a small amount of concentrated hydrochloric acid, it yields a mixture of two *p*-benzoylaminophenyl mercaptans. The colourless modification, $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{SH}$, is obtained by adding hydrochloric acid to the cold alkaline solution of the mixture; it crystallises in small leaflets, commences to sinter at 165° , melts at 180° , gives precipitates with lead acetate and silver nitrate, and on oxidation with ferric chloride or potassium ferrocyanide and sodium hydroxide yields dithiobenzanilide. The yellow modification, obtained by heating the colourless form or by crystallising it from alcohol,

forms large, yellow needles and melts at 182° . Both modifications form colourless solutions.

The structure of these isomeric modifications of the acylamino-phenyl mercaptans is discussed. G. Y.

Conversion of α -Nitro- β -phenyl- α -methylcarbamide into s -Nitrophenylmethylcarbamide. ROLAND SCHOLL and B. NYBERG (*Ber.*, 1906, 39, 2491—2494. Compare Scholl and Holdermann, *Annalen*, 1906, 345, 382).—The additive compound obtained from methylnitroamine and phenylcarbimide has the formula $\text{NHPh}\cdot\text{CO}\cdot\text{NMe}\cdot\text{NO}_2$, for by treatment at 0° with concentrated sulphuric acid a mixture of s -o-nitrophenylmethylcarbamide and p -nitrophenylmethylcarbamide is obtained, and is separated by hot 1 per cent. sodium hydroxide solution, in which the former compound is more easily soluble. The orientation of the NO_2 group is determined by heating the compounds with hydrochloric acid at 120 — 130° , whereby o - and p -nitroaniline respectively are obtained.

α -Nitro- β -phenyl- α -methylcarbamide yields with phenol at 100° *phenyl phenylcarbamate*, which forms colourless needles and melts at 125.5° ; with aniline, it forms s -diphenylcarbamide. C. S.

Unsaturated Disulphides. EMIL FROMM (*Annalen*, 1906, 348, 144—160. Compare Abstr., 1895, i, 605; Hantzsch and Wolvekamp, Abstr., 1904, i, 718).—Disulphides which are decomposed with separation of sulphur on heating or on treatment with water, alkalis, ammonia, or amines, contain the grouping $-\ddot{\text{C}}\cdot\text{S}\cdot\text{S}\cdot\ddot{\text{C}}-$, and are not necessarily cyclic disulphides. The double linkings may connect the carbon atoms with similar atoms or groups, as in ethyl dioxothiocarbonate, $\text{S}\cdot\text{C}(\text{OEt})\cdot\text{S}\cdot\text{S}\cdot\text{C}(\text{OEt})\cdot\text{S}$, dibenzoyl sulphide, $\text{O}\cdot\text{CPh}\cdot\text{S}\cdot\text{S}\cdot\text{CPh}\cdot\text{O}$, or phenylthiouret, $\text{NH}\langle\begin{smallmatrix} \text{C}(\text{NPh}) \\ \text{C}(\text{NH}) \end{smallmatrix}\rangle\text{S}_2$, or with dissimilar atoms or groups,

as in perthiocyanic acid, $\text{NH}\langle\begin{smallmatrix} \text{C}(\text{NH}) \\ \text{C}(\text{S}) \end{smallmatrix}\rangle\text{S}_2$. The reaction is often complicated by the interaction of the primary products. If the double linkings are part of stable ring systems, as in diphenyl disulphide, $\text{SPh}\cdot\text{SPh}$, or the thiodiazolone disulphides (Busch, Abstr., 1896, i, 190), the decomposition by means of alkalis takes place, but without separation of sulphur. Disulphides which do not contain the above grouping are stable towards alkalis.

The author discusses the constitution of the sulphides and oxides of the thiocarbimides which, as represented by Freund (Abstr., 1895, i, 576), form exceptions to this rule. G. Y.

Dithiobiurets. EMIL FROMM and KURT SCHNEIDER (*Annalen*, 1906, 348, 161—174. Compare Fromm, Abstr., 1893, i, 575).—Perthiocyanic acid reacts with p -toluidine, o -toluidine, as - m -xylylidine, and o -phenetidine, forming the thiobiurets, thiocarbamides, and sulphur. The dithiobiurets, which are isolated by extraction with cold dilute alkali hydroxides, are oxidised by iodine, forming the thiourets, which are bases, and when heated with concentrated hydrochloric acid at 165° yield 2-aminobenzothiazoles.

p-Tolyldithiobiuret melts at 173.5° (159° ; Tursini, Abstr., 1884, 1140) and forms *p*-tolylthioureth hydriodide, $\text{NH} \begin{array}{c} \text{C}(\text{N} \cdot \text{C}_7\text{H}_7) \cdot \text{S} \\ \text{C}(\text{NH}) \text{---} \text{S} \end{array} \text{HI}$, separating in yellow crystals and melting at 221.5° . Contrary to Tursini's statement (*loc. cit.*), *p*-tolyldithiobiuret reacts with 1 mol. of methyl iodide to form *methyl-p-tolyl-ψ-dithiobiuret*, $\text{C}_{10}\text{H}_{13}\text{N}_3\text{S}_2$, which crystallises in nodular aggregates of needles and melts at 125.5° . With 2 mols. of methyl iodide, it forms *dimethyl-p-tolyl-ψ-dithiobiuret*, $\text{C}_7\text{H}_7 \cdot \text{N} \cdot \text{C}(\text{SMe}) \cdot \text{NH} \cdot \text{C}(\text{SMe}) \cdot \text{NH}$, which crystallises in white needles, melts at 67° , and evolves mercaptan at 100° . When treated with acetone and hydrogen chloride, this forms *methyl-p-tolyldimethyl-ψ-dithioketuret*, $\text{C}_6\text{H}_4\text{Me} \cdot \text{N} \cdot \text{C}(\text{SMe}) \cdot \text{N} \begin{array}{c} \text{C}(\text{SMe}) \\ \text{CMe}_2 \end{array} \text{N}$, which crystallises in white needles and melts and decomposes at 164° . *p-Tolyl-ψ-thiobenzylcyanocarbamide*, $\text{C}_7\text{H}_7 \cdot \text{NH} \cdot \text{C}(\text{SC}_7\text{H}_7) \cdot \text{N} \cdot \text{CN}$, prepared by heating *p*-tolyldithiobiuret with sodium hydroxide and benzyl chloride in alcoholic solution, crystallises in glistening, white scales and melts at 181.5° .

o-Tolyldithiobiuret, $\text{C}_9\text{H}_{11}\text{N}_3\text{S}_2$, crystallises in stout needles and melts at 159° . *o-Tolylthioureth hydriodide*, $\text{C}_9\text{H}_9\text{N}_3\text{S}_2\text{HI} \cdot \text{C}_2\text{H}_6\text{O}$, crystallises from alcohol in yellow needles and melts at 153° . *o-Tolyl-ψ-thiobenzylcyanocarbamide*, $\text{C}_{16}\text{H}_{16}\text{N}_3\text{S}$, forms a white, crystalline powder and melts at 165° .

m-Xylyldithiobiuret, $\text{C}_{10}\text{H}_{13}\text{N}_3\text{S}_2$, forms yellow crystals and melts at about 129° . *m-Xylylthioureth hydriodide*, $\text{C}_{10}\text{H}_{11}\text{N}_3\text{S}_2\text{HI}$, crystallises in yellow needles and melts at 146° .

o-Methoxyphenyldithiobiuret, $\text{C}_{10}\text{H}_{13}\text{ON}_3\text{S}_2$, forms long, yellow needles and melts at 153° . *o-Methoxyphenylthioureth hydriodide*,



forms stout, yellow needles and melts at $181\text{--}182^{\circ}$; the *hydrochloride* forms yellow needles and melts at 205° . G. Y.

Action of Alkali Hydroxides and Alkylloxides on Unsaturated Imides. ARNALDO PIUTTI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 79—87).—The violet coloration given by *p*-methoxyphenylcitraconimide and other analogous imides (Abstr., 1889, 590) depends on the formation of an additive compound of the alkali or alkaline-earth hydroxide or their alkylloxides or acetates with the imide itself, a compound which is transformed by moisture into a salt of *p*-methoxyphenylcitraconamic acid. T. H. P.

Preparation of Phenols and their Substitution Products. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (D.R.-P. 167211).—The replacement of a diazonium complex by a hydroxyl group is a reaction which does not always proceed smoothly, and the following process has been found to give favourable results. The solutions of the diazonium salts derived from *o*-anisidine, *o*- and *p*-aminophenols, and *o*-toluidine are introduced into a boiling 50 per cent. solution of copper sulphate. The guaiacol and *o*-cresol produced from *o*-anisidine and *o*-toluidine respectively are distilled in steam, whilst the catechol and quinol

obtained from the aminophenols are extracted with ether. From 1.2 to 5 parts of copper sulphate are employed to one of the aromatic amine.
G. T. M.

Behaviour of Trinitrobenzene Derivatives with Cyclic Amines. E. O. SOMMERHOFF (*Zeit. Farb. Ind.*, 1906, 5, 270—271).—In connection with von Georgievics' view that picric acid is capable of existing in two differently coloured forms (this vol., i, 420), it is pointed out that on moistening picric acid with aniline a red colour is first developed which changes to yellow as the ordinary picrate is formed. With dimethylamine in alcoholic solution, picric acid gives the yellow picrate at once, but in benzene solution a transient red coloration is observed. The additive compounds described in conjunction with Noelting (this vol., i, 157) are referred to, and the author is led to dissent from von Georgievics' theoretical views.
W. A. D.

***p*-Aminodiphenyl Oxide-3-sulphonic Acid.** AKTIENGESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 169357).—When *p*-aminodiphenyl oxide is sulphonated with concentrated sulphuric acid at 80—100°, a sulphonic acid is produced containing the sulpho-group in the unsubstituted ring, but when the acid sulphate of *p*-aminodiphenyl oxide is baked at 180° the sulpho-group enters an ortho-position with respect to the amino-group. The new *p*-aminodiphenyl oxide 3-sulphonic acid yields valuable lake-forming azo-colouring matters; the free acid and its sodium, calcium, and copper salts are only sparingly soluble in water.
G. T. M.

***p*-Hydroxyphenylglycinamide.** AKTIENGESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 166799).—*p*-Hydroxyphenylglycinamide,

$$\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2,$$
 is obtained by condensing chloroacetamide with *p*-aminophenol in the presence of substances capable of fixing hydrogen chloride; an excess of *p*-aminophenol would answer this purpose. For use as a photographic developer, the *p*-hydroxyphenylglycinamide is dissolved in 200 parts of water containing 5 parts of potassium carbonate and 5 parts of anhydrous sodium sulphite.
G. T. M.

Derivatives of 3-Amino-*p*-cresol-5-sulphonic Acid. KALLE & Co. (D.R.-P. 168857).—3-Amino-*p*-cresol-5-sulphonic acid is readily acetylated when dissolved in water and the solution exactly neutralised, and the acetyl derivative when nitrated below 5° with a mixture of concentrated nitric and sulphuric acids yields a well-defined, crystalline nitro-derivative, which is readily hydrolysed on boiling with hydrochloric acid. The nitro-3-amino-*p*-cresol-5-sulphonic acid which is thus obtained in a crystalline condition furnishes an azo- β -naphthol having valuable tinctorial properties.
G. T. M.

Preparation of 3-Amino-2-hydroxybenzylamine. ALFRED EINHORN (D.R.-P. 167572).—3-Nitro-2-hydroxybenzylamine, when reduced with tin and hydrochloric acid, furnishes 3-amino-2-hydroxybenzylamine; this substance, which is a valuable photographic developer,

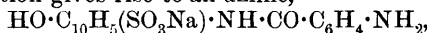
may also be prepared by reducing benzoyl-3-nitro-2-hydroxybenzylamine to *ω*-benzoyl-3-amino-2-hydroxybenzylamine, a base which crystallises in colourless needles melting at 186°, and then hydrolysing this product with concentrated hydrochloric acid. 3-Amino-2-hydroxybenzylamine furnishes a soluble dihydrochloride crystallising in colourless needles; it develops a violet coloration with ferric chloride, precipitates silver from Tollens' solution, sets free gold from its salts, giving rise to a violet coloration, and forms crystalline platini- and stanni-chlorides.

G. T. M.

Preparation of 4-Chloro-*α*-naphthol. KALLE & Co. (D.R.-P. 167458).—*α*-Naphthol is conveniently chlorinated by slowly adding to its cold alkaline solution one molecular proportion of sodium hypochlorite also dissolved in aqueous sodium hydroxide. The addition of dilute acetic or hydrochloric acid liberates 4-chloro-*α*-naphthol, which first separates as an oil and then solidifies in aggregates of needles. The product after distillation in superheated steam or crystallisation in light petroleum melts at 64–65°, and the yield is extremely good.

G. T. M.

Preparation of Aminoarylacylaminonaphtholsulphonic Acids. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 170045).—The aminonaphtholsulphonic acids readily react in aqueous solution at moderate temperatures with the chlorides of the nitro- and acetyl-amino-acids of the aromatic series. Thus sodium 6-amino-*α*-naphthol-3-sulphonate condenses with *m*-nitrobenzoyl chloride in neutral aqueous solution in the presence of sodium acetate to form the compound $\text{HO}\cdot\text{C}_{10}\text{H}_5(\text{SO}_3\text{Na})\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, and this substance on reduction gives rise to an amine,



which combines with diazonium salts to produce azo-colouring matters capable of being again diazotised and condensed on the fibre. Similarly, sodium 6-amino-*α*-naphthol-3-sulphonate combines with acetylaminobenzoyl and benzenesulphonic chlorides, and the products when hydrolysed also give rise to aminosulphonic acids which are used in the production of ingrain azo-dyes.

G. T. M.

Condensation Products of *α*-Naphthol and Benzophenone Chloride. ALBERT G. SHRIMPTON (*Chem. News*, 1906, 94, 13–14. Compare McKenzie, *Trans.*, 1896, 69, 985; 1901, 79, 1204).—*Diphenyldihydroxydi-α-naphthylmethane*, $\text{CPh}_2(\text{C}_{10}\text{H}_6\cdot\text{OH})_2$, obtained when benzophenone chloride is heated with *α*-naphthol, forms microscopic crystals which darken at 204°, and ultimately melt to a brown, viscid liquid at 208.2–209.2°. When heated with sodium acetate and acetic anhydride in a reflux apparatus, it yields small, silky-white needles and plates melting at 202°, of uncertain composition. When the reaction between *α*-naphthol and benzophenone chloride is moderated by the presence of a considerable amount of light petroleum, a product is obtained which, when recrystallised from acetone, forms slender, yellow, microscopic prisms melting at 180.5–181°.

D. A. I.

Diisoapiole, Diisoeugenol Methyl Ether, and Diasarone. TIBOR SZÉKI (*Ber.*, 1906, 39, 2422—2424. Compare Tiemann, *Abstr.*, 1892, 45; Angeli and Mola, *Abstr.*, 1895, i, 24).—*Diisoapiole*, $C_{24}H_{28}O_3$, prepared by treating *isoapiole* with hydrogen chloride in ethereal solution, evaporating off the ether, and heating the residual oil at 200° in a sealed tube, forms white crystals and melts at 97° .

Diisoeugenol methyl ether, $C_{22}H_{26}O_4$, formed by the action of hydrogen chloride on *isoeugenol methyl ether* in ethereal solution, crystallises in snow-white, glistening needles and melts at 106° .

Diasarone, $C_{24}H_{32}O_6$, formed in the same way from *asarone*, crystallises from alcohol in white needles and melts at 100° .

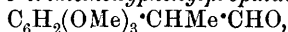
These three polymerisation products are readily soluble in the usual solvents, and do not form additive compounds with bromine.

In one experiment the *diasarone* was accompanied by *s-di-trimethoxyphenylethylene*, $C_2H_2[C_6H_2(OMe)_3]_2$, which forms white crystals, melts at 96° , and forms an *additive* compound with bromine.

G. Y.

Derivatives of Asarone. TIBOR SZÉKI (*Ber.*, 1906, 39, 2419—2421).—*Dihydroasarone*, $C_6H_2Pr^a(OMe)_3$, prepared by reducing *asarone* with sodium in alcoholic solution, is obtained as an aromatic, colourless oil, which boils at 185 — 188° under 40 mm. pressure, and is miscible with alcohol, ether, benzene, or glacial acetic acid.

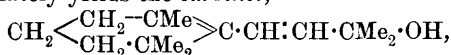
Asarone dibromide (Rizza and Butleroff, *Abstr.*, 1884, 1042), prepared by the action of bromine on *asarone* in carbon disulphide solution, melts at 83° , and when boiled with sodium ethoxide in alcoholic solution, yields an impure oil having an unpleasant odour. When treated with mercuric oxide and iodine in cooled alcoholic solution, *asarone* yields α -2:4:5-trimethoxyphenylpropaldehyde,



which is an oil boiling at 275° under the ordinary pressure.

G. Y.

Preparation of Tertiary Alcohols. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 166898, 166899).—By the action of excess of organic magnesium haloids ($MgRBr, Et_2O$) on the carboxylic acids or their metallic salts, additive products are obtained, which on treatment with water or acid give rise to a tertiary alcohol. Thus the ethereal solutions of magnesium ethyl bromide and benzoic acid when slowly mixed in the cold evolve ethane and give a precipitate which dissolves completely in dilute ice-cold sulphuric acid. The ethereal extract of this solution furnishes phenyldiethylcarbinol, $C_{Et_2}Ph \cdot OH$, which boils at 110° under 12 mm. pressure. *cyclo*Citrylideneacetic acid, when treated in this way with magnesium methyl bromide, ultimately yields the *carbinol*,

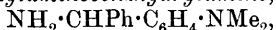


which boils at 130° under 12 mm. pressure; methane is evolved during the initial stage of the reaction. In this operation dry sodium *cyclo*-citrylideneacetate may be substituted for the free acid, and in a similar manner anhydrous sodium benzoate may be employed in the preparation of phenyldiethylcarbinol.

G. T. M.

Preparation of *p*-Dialkylaminobenzhydrylamines. EMANUEL MERCK (D.R.-P. 167053).—The oximes, phenylhydrazones, and semicarbazides of the *p*-dialkylaminobenzophenones ($\text{COPh}\cdot\text{C}_6\text{H}_4\cdot\text{NR}_2$), when reduced electrically or in neutral acid or alkaline solution with the help of sodium or sodium amalgam, give rise to the *p*-dialkylaminobenzhydrylamines.

p-Dimethylaminobenzophenoneoxime crystallises in colourless prisms melting at $152\text{--}154^\circ$, and when reduced with sodium and ethyl alcohol yields *p*-dimethylaminobenzhydrylamine,



which forms colourless, acicular crystals and melts at $82\cdot5^\circ$; the hydrochloride separates in sparingly soluble leaflets melting at $186\text{--}187^\circ$.

p-Diethylaminobenzophenoneoxime crystallises in colourless needles melting at $175\text{--}177^\circ$; the corresponding hydrazone is oily.

p-Diethylaminobenzhydrylamine, $\text{NH}_2\cdot\text{CHPh}\cdot\text{C}_6\text{H}_4\cdot\text{NEt}_2$, separates in colourless needles melting at $120\text{--}121^\circ$; its hydrochloride, which is obtained in voluminous aggregates of needles, is sparingly soluble in cold water. These dialkylaminobenzhydrylamines form a new class of anaesthetics.

G. T. M.

Preparation of *p*-Dialkylaminobenzhydrylamines. EMANUEL MERCK (D.R.-P. 167462, 167463).—Dimethylaminobenzhydrylamine may be obtained by heating either dimethylaminobenzhydrol, the ethyl ether of this substance, or diethylaminodiphenylbromomethane with ammonia under pressure at $150\text{--}200^\circ$; it can also be prepared by heating the last of these three compounds with potassium phthalimide at 180° , and then eliminating phthalic acid from the intermediate product by digestion in an autoclave with aqueous alcoholic ammonia at 140° .

G. T. M.

Reduction of Aromatic Carbinols. AUGUST KLAGES (*Ber.*, 1906, 39, 2587—2595).—[With ERNST LAUCK and KARL GIESER.]—The reduction of cinnamyl alcohol by sodium and alcohol yields a mixture of propenylbenzene, $\text{CHPh}\cdot\text{CHMe}$, and propylbenzene; the former compound was identified by oxidising it to benzoic acid. α -Phenylallyl alcohol (this vol., i, 638), with the same reducing agent, yields a mixture of allylbenzene and propylbenzene, which, after treatment with alcoholic potash at 130° , contains propenylbenzene, identified in the form of its bromide.

α -Phenyl- Δ^α -butene- γ -ol is conveniently obtained by decomposing the reaction product of magnesium methyl bromide and cinnamaldehyde with an ice-cold solution of ammonium chloride. It boils at 131° under 12 mm. pressure, and by reduction with sodium and alcohol yields a mixture of butylbenzene and α -phenyl- Δ^β -butylene.

α -Phenyl- Δ^α -pentene- γ -ol, $\text{CHPh}\cdot\text{CH}\cdot\text{CHEt}\cdot\text{OH}$, obtained like the preceding alcohol from magnesium ethyl bromide, is a colourless oil which boils at 138° under 11.5 mm. pressure, and is reduced by sodium and alcohol to α -phenyl- Δ^β -pentene, $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CHEt}$, a colourless, mobile oil with a peculiar odour, which boils at 80° under 12 mm. pressure, has a sp. gr. $0\cdot8837$ at $16^\circ/4^\circ$, n_D $1\cdot5059$ at 16° , and

forms an oily *bromide*, $C_{11}H_{14}Br_2$. When this hydrocarbon is heated with alcoholic potash at 150° for one day it is changed into α -phenyl- Δ^{α} -pentene, $CHPh:CHPr^a$, which boils at 82° under 9 mm. pressure, has a sp. gr. 0.892 at $15^\circ/4^\circ$, n_D 1.5139 at 15° , and forms a *bromide*, $C_{11}H_{14}Br_2$, which separates from alcohol in colourless leaflets and melts at 61° .

α -Phenyl- γ -methyl- Δ^{α} -butene- γ -ol, $CHPh:CH \cdot CMe_2 \cdot OH$, is obtained by decomposing the reaction product of magnesium methyl bromide and benzylideneacetone with ice and ammonium chloride; it melts at 38.5° , boils at 123 — 124° under 11 mm pressure, and is reduced by sodium and alcohol to α -phenyl- γ -methyl- Δ^{β} -butylene (Abstr., 1904, i, 569).

α -Phenyl- γ -methyl- Δ^{α} -pentene- γ -ol, $CHPh:CH \cdot CMeEt \cdot OH$, obtained like the preceding alcohol from magnesium ethyl bromide, boils at 124 — 125° under 11 mm. pressure, and is not reduced by sodium and alcohol.

α -Phenyl- γ -methyl- $\Delta^{\alpha\gamma}$ -pentadiene, $CHPh:CH \cdot CMe:CHMe$, obtained by decomposing the reaction product of magnesium ethyl iodide (2 mols.) and benzylideneacetone (1 mol.) with ice and dilute sulphuric acid, boils at 130° under 20 mm. pressure, has a sp. gr. 0.9593 at $19^\circ/4^\circ$, n_D 1.5366, and is reduced by sodium and alcohol to α -phenyl- γ -methyl- Δ^{β} -pentene, $CH_2Ph:CH:CHMeEt$, a colourless, mobile oil which boils at 119 — 120° under 20 mm. and at 226° under 749 mm. pressure, has a sp. gr. 0.9014 at $18^\circ/4^\circ$, n_D 1.5100, and forms a *nitrosylchloride*, which melts at 151° .

Carbinols of the type $CPh:C \cdot CHR \cdot OH$ (where R = alkyl) are obtained from magnesium alkyl haloids and either phenylpropargyl-aldehyde or α -bromocinnamaldehyde; in the latter case the intermediate brominated alcohol must be boiled with alcoholic potash.

α -Phenyl- α -butinene- γ -ol, $CPh:C \cdot CHMe \cdot OH$, obtained by the second method, is a colourless oil which boils at 121 — 122° under 9 mm. pressure, and is reduced by sodium and alcohol to a mixture of Δ^{β} -butenylbenzene and a small quantity of butylbenzene.

α -Phenyl- α -pentinene- γ -ol, $CPh:C \cdot CHEt \cdot OH$, obtained by the first method, boils at 133 — 134° under 10.5 mm. pressure, has a sp. gr. 1.018 at $15.5^\circ/4^\circ$, n_D 1.5570 at 15.5° , and forms a heavy oily *bromide*, $C_{11}H_{12}Br_2$, with hydrogen bromide in glacial acetic acid. When the acetylenic alcohol is prepared by the second method, the intermediate β -bromo- α -phenyl- Δ^{α} -pentene- γ -ol, $CHPh:CBr \cdot CHEt \cdot OH$, boils at 146 — 147° under 11 mm. pressure, has a sp. gr. 1.3533 at $17^\circ/4^\circ$, and n_D 1.5840 at 17° . The reduction of the acetylenic alcohol by sodium and alcohol yields the Δ^{β} -pentenylbenzene described above. C. S.

Migration of the Phenyl Group in the Halohydrins and the α -Glycols. MARC TIFFENEAU (*Compt. rend.*, 1906, 142, 1537—1539. Compare Abstr., 1902, i, 666; 1904, i, 63, 133).— $\beta\beta$ -Diphenylethylene glycol, $OH \cdot CPh_2 \cdot CH_2OH$, prepared by the action of magnesium phenyl bromide on ethyl glycolate, is converted quantitatively into diphenylacetaldehyde, $CHPh_2 \cdot CHO$, by the action of sulphuric acid, and α -phenylpropylene- $\alpha\beta$ -glycol, $OH \cdot CHPh \cdot CHMe \cdot OH$ (compare

Zincke, Abstr., 1884, 1003), is converted similarly into phenylacetone, $\text{CH}_3\text{Ph}\cdot\text{CO}\cdot\text{CH}_3$.

The transformation of the substituted α -glycols into the corresponding aldehyde or ketone by the action of sulphuric acid does not therefore involve the migration of a phenyl group except in the case of hydrobenzoin, whilst in the similar transformation of the corresponding iodohydrins by means of silver nitrate the change is always accompanied by the migration of a phenyl group. M. A. W.

Cholesterol. II. Specific Rotations of Cholestene and Cholestane Derivatives. JULIUS MAUTHNER (*Monatsh.*, 1906, 27, 421—431. Compare this vol., i, 579; Mauthner and Suida, Abstr., 1894, i, 326, 486; 1896, i, 425; 1897, i, 31; 1903, i, 625; Windaus, Abstr., 1904, i, 49, 667; this vol., i, 174, 579, 580; Diels and Abderhalden, this vol., i, 272).—The author has determined the influence of the addition of halogens and of hydrogen haloids on the specific rotations of cholesterol, cholestene, and cholestane. The substances were dissolved in ether, alcohol, or chloroform.

Cholesterol has $[\alpha]_D - 29.92^\circ$, the hydrochloride $[\alpha]_D + 5.7^\circ$, the dichloride $[\alpha]_D - 29.1^\circ$, and the dibromide $[\alpha]_D - 41.6^\circ$. Cholestanonol has $[\alpha]_D - 3.14^\circ$.

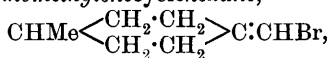
Cholesteryl acetate has $[\alpha]_D - 29.8^\circ$, its dichloride $[\alpha]_D - 32.8^\circ$, and its dibromide $[\alpha]_D - 45.1^\circ$.

Cholesteryl chloride has $[\alpha]_D - 26.36^\circ$; the hydrochloride [β -dichlorocholestane] has $[\alpha]_D + 20.1^\circ$ in benzene solution or $+12.16^\circ$ in ethereal solution. Trichlorocholestane has $[\alpha]_D - 34.7^\circ$. Cholesteryl chloride dibromide, which melts at 130 — 131° , has $[\alpha]_D - 55.0^\circ$.

Cholestene hydrochloride [chlorocholestane] has $[\alpha]_D + 21.8^\circ$, and cholestene dichloride [α -dichlorocholestane] $[\alpha]_D - 28.7^\circ$.

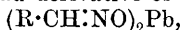
α -Cholestene dibromide (Mauthner and Suida, Abstr., 1894, i, 326) melts at 145 — 146° and has $[\alpha]_D + 48.9^\circ$. β -Cholestene dibromide immediately after solution in chloroform has $[\alpha]_D - 39.6^\circ$, after twenty-four hours $[\alpha]_D \pm 0^\circ$, and at the end of some days $[\alpha]_D + 39.4^\circ$. The last specific rotation is not increased beyond $+40^\circ$ on heating the solution in a sealed tube at 65° for one hour, but on evaporation the α -dibromide is obtained. The change in the rotation takes place much more slowly in benzene solution. The dibromocholestanes are probably alicyclic *cis-trans*-isomerides. G. Y.

4-Methylcyclohexylidene-1-acetic Acid. WILLY MARCKWALD and RICHARD METH (*Ber.*, 1906, 39, 2404—2405. Compare this vol., i, 360, 584).—When treated with bromine in aqueous sodium carbonate solution, 4-methylcyclohexylidene-1-acetic acid, melting at 40.5 — 41° , yields 1-methyl-4-bromomethylenecyclohexane,



which, when heated with water at 140 — 150° , forms hexahydro-*p*-tolualdehyde (Wallach and Evans, this vol., i, 566). Perkin and Pope's acid melting at 88° (*Proc.*, 1906, 22, 107) is probably 4-methyl- Δ^1 -cyclohexene-1-acetic acid, $\text{CHMe} \begin{array}{c} \text{CH}_2 - \text{CH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ (compare Rupe, Ronus, and Lotz, Abstr., 1903, i, 139). G. Y.

Conversion of Aldoximes into Nitriles. WALTHER BORSCHÉ (*Ber.*, 1906, **39**, 2503).—If 2 mols. of an aldoxime are heated with 1 mol. of lead oxide, the lead derivative of the aldoxime,



is formed, and on further heating is decomposed into lead oxide, water, and the nitrile. The violence of the action is moderated by mixing the reacting substances with an amount of sand two to three times the weight of the aldoxime. Nitriles have been prepared in this manner from benzaldoxime, anisaldoxime, cuminaldoxime, heptaldoxime, and furfuraldoxime. G. Y.

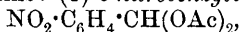
Crystallographic Study of New Organic Compounds. FRANCESCO RANFALDI (*Atti R. Accad. Lincei*, 1906, [v], **15**, i, 715—724).—Sodium 2-*o*-nitro-*p*-toluidino-3:5-dinitrobenzoate (Cuttitta, *Rend. Soc. Chim. Roma*, 1905, 146) crystallises in the triclinic system [$a:b:c = 1.52579:1.094494$; $\alpha = 76^\circ 11'$, $\beta = 81^\circ 27'$, $\gamma = 93^\circ 29'$].

The corresponding pyridine salt (Cuttitta, *loc. cit.*) crystallises in the triclinic system [$a:b:c = 1.35414:1.109430$; $\alpha = 87^\circ 16'$, $\beta = 76^\circ 36'$, $\gamma = 92^\circ 14'6''$].

i-Lupanine platinichloride (Soldaini, *Abstr.*, 1892, 892) crystallises in the monoclinic system [$a:b:c = 2.6124:1:1.3428$; $\beta = 83^\circ 46'33''$].

Ethyl naphthalate (Errera), $C_{10}H_8(CO_2Et)_2$, melting at $58-60^\circ$, crystallises in the monoclinic system [$a:b:c = 1.0555:1:3.1814$; $\beta = 70^\circ 45'27''$]. T. H. P.

Products of Dehydration of Phenyl-*o*-nitrocinnamic Acid and the Products which accompany this Acid when prepared by Perkin's Synthesis. MARUSSIA BAKUNIN and L. PARLATI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], **12**, 18—34).—When sodium phenylacetate, *o*-nitrobenzaldehyde, and acetic anhydride are heated at 120° , α -phenyl-*o*-nitrocinnamic acid is formed and less resin is obtained than at 160° . The portion of the product insoluble in sodium carbonate solution contains: (1) *o*-nitrobenzylidene diacetate,



which crystallises from light petroleum in small, yellow prisms melting at $89-90^\circ$, dissolves in most solvents, and is slightly decomposed by a solution of phenylhydrazine, giving *o*-nitrobenzaldehyde phenylhydrazone; (2) *phenyl-o-nitrophenylacrylene* (?) [*phenyl-o-nitrophenylenethylene*],

$NO_2 \cdot C_6H_3 \cdot \begin{smallmatrix} CH \\ | \\ CPh \end{smallmatrix}$, which crystallises from ethyl acetate in ruby-red, shining, rhombic laminae

$$[a:b:c = 0.68275:1:1.04489]$$

and melts at $186-187^\circ$.

Ethyl phenyl-o-nitrocinnamate, obtained by the action of alcohol on the acid, separates from light petroleum in yellow, monoclinic prisms melting at 59° and is soluble in alcohol.

Phenylhydrazine phenyl-o-nitrocinnamate, $C_{15}H_{11}O_4N \cdot NHPh \cdot NH_2$, crystallises from benzene in tufts of silky, yellow, unstable needles and melts at $97-103^\circ$.

Phenyl-o-nitrocinnamoyl phenylhydrazide, $C_{21}H_{17}O_3N_3$, prepared by the action of excess of phenylhydrazine on phenyl-o-nitrocinnamic anhydride, crystallises from alcohol in shining, yellow laminae melting at 167° . It is accompanied by a small quantity of a yellow powder, infusible at 300° , the nature of which has not been determined.

Phenyl-o-nitroindone phenylhydrazone, $C_{15}H_9O_2N:N_2HPh$, crystallises from benzene in canary-yellow, silky needles melting at 135 – 136° . The *oxime*, $C_{15}H_{10}O_2N:NOH$, crystallises from benzene in silky, orange-yellow needles melting at 246 – 248° . T. H. P.

Action of Sodium Hypochlorite and of Bromine and Sodium Alkyl oxides on Hydrocinnamamide. R. A. WEERMANN and W. J. A. JONGKEES (*Rec. trav. chim.*, 1906, **25**, 238–243).—Hydrocinnamamide (1 mol.) reacts with sodium hypochlorite (1 mol.) and sodium hydroxide ($\frac{1}{2}$ mol.) at the ordinary temperature to form *s*- β -diphenylethylcarbamide; if, however, the quantity of sodium hydroxide is increased and the temperature is raised to 80° , β -diphenylethylamine is obtained.

Hydrocinnamamide reacts with bromine and sodium ethoxide or methoxide at the boiling point of the alcohol to form the corresponding alkyl ester of β -phenylethylaminoformic acid; ethyl benzylaminoformate, similarly prepared from phenylacetamide, melts at 44° , and *methyl benzylaminoformate* crystallises in thin needles from light petroleum and melts at 64 – 65° . M. A. W.

Formation of Salicylic Acid from Sodium Phenoxide. JACOB MOLL VAN CHARANTE (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, **9**, 20–23).—On heating sodium phenyl carbonate in a sealed tube at 100° , carbon dioxide and phenol are formed along with small amounts of sodium salicylate. Sodium phenoxide crystallises from acetone with 1 mol. of the solvent in long, soft, and almost white needles. When sodium phenyl carbonate is placed in dry acetone, it yields carbon dioxide, phenol, and a mixture of normal and acid sodium carbonates. Sodium salicylate crystallises from acetone in small needles containing $\frac{1}{2}$ to 1 mol. of the solvent, whereas disodium salicylate is insoluble in acetone. E. F. A.

Bismuth Disalicylate. CHEMISCHE FABRIK VON HEYDEN, AKTIEN-GESELLSCHAFT (D.R.-P. 168408).—The "*bismuthum salicylicum basicum*" or "*bismuthum subsalicylicum*" of commerce is the monosalicylate of bismuth having the formula $OH \cdot C_6H_4 \cdot CO \cdot O \cdot BiO$. The so-called neutral bismuth salicylate is a mixture of a basic salt and free salicylic acid. *Bismuth disalicylate*, $OH \cdot Bi(O \cdot CO \cdot C_6H_4 \cdot OH)_2$ or $O[Bi(O \cdot CO \cdot C_6H_4 \cdot OH)_2]_2$, has now been prepared by adding crystallised bismuth nitrate to an aqueous solution of sodium salicylate, and, after thorough mixing, extracting the free salicylic acid at the ordinary temperature with either dilute ammonia or indifferent solvents such as alcohol, ether, or chloroform. The product is a white, almost tasteless powder, which has a neutral reaction in cold water, but is decomposed on warming into the monosalicylate and free salicylic acid.

G. T. M.

Action of Chloroform and Sodium Hydroxide on Phenols in Acetone Solution. GUIDO BARGELLINI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 579—587).—The compound, $C_{10}H_{12}O_3$, which was obtained by Link (D.R.-P. 80986) by heating an acetone solution of phenol with chloroform and sodium hydroxide, and was regarded by this author as hydroxyphenyl hydroxyisopropyl ketone or hydroxyisobutyrylphenol, $OH \cdot C_6H_4 \cdot CO \cdot CMe_2 \cdot OH$, exhibits none of the reactions of phenols or ketones, whilst it contains a carboxyl group; it must hence be assumed to be α -phenoxyisobutyric acid, $OPh \cdot CMe_2 \cdot CO_2H$, and it agrees in properties with the data given by Bischoff (Abstr., 1900, i, 345) for this compound. The corresponding naphthol derivatives described by Link are identical with the α - and β -naphthoxyisobutyric acids prepared by Bischoff (Abstr., 1900, i, 395).

By the action of chloroform, sodium hydroxide, and acetone on *o*- or *p*-cresol or thymol, the author has obtained compounds identical with those prepared by Bischoff (Abstr., 1900, i, 392 and 394) by the action of ethyl α -bromoisobutyrate on the sodium derivatives of *o*- or *m*-cresol or thymol.

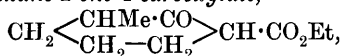
The views of Link concerning these compounds (compare Beilstein, Handbuch, III, Suppl., 120 and 143) are hence erroneous.

The first phase in the reaction is probably the formation of acetone-chloroform (which may, indeed, be used in place of the chloroform), this being then acted on by sodium hydroxide in presence of acetone, yielding α -hydroxyisobutyric acid, which, with the phenol, gives α -phenoxyisobutyric acid. The chloroform may also be replaced by bromoform, bromal, chloral, or carbon tetrachloride or tetrabromide.

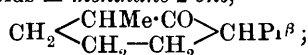
The compounds prepared by the author have all been described previously.

T. H. P.

Syntheses by means of the Carboxylic Esters of Cyclic Ketones. II. Synthesis of *m*-Menthane-2-one and of *m*-Menthane-4-one from 1-Methylcyclohexane-2-one and 1-Methylcyclohexane-4-one. ARTHUR KÖTZ and A. MICHELS (*Annalen*, 1906, 348, 91—96. Compare Kötz and Hesse, this vol., i, 88).—When distilled under reduced pressure, ethyl 3-methylcyclohexane-2-one-1-oxalate, $CH_2 \begin{smallmatrix} \text{CHMe} \cdot \text{CO} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} > CH \cdot CO \cdot CO_2Et$, prepared by the action of ethyl oxalate and sodium on 1-methylcyclohexane-2-one in presence of light petroleum, loses carbon monoxide and yields ethyl 3-methylcyclohexane-2-one-1-carboxylate,



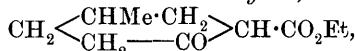
which boils at 115° under 12 mm. pressure and forms a semicarbazone, $C_{11}H_{19}O_3N_3$, melting at 140° . With isopropyl iodide and sodium ethoxide it forms ethyl 3-methyl-1-isopropylcyclohexane-2-one-1-carboxylate, $C_6H_7OMePr^i \cdot CO_2Et$, which boils at 128° under 10 mm. pressure, forms a semicarbazone only slowly, and on hydrolysis and elimination of carbon dioxide yields *m*-menthane-2-one,



this boils at 82° under 10 mm. pressure, has a sp. gr. 0·9128 at 15°, and reacts slowly with semicarbazide.

The following substances have been prepared in the same manner, starting from 1-methylcyclohexane-4-one.

Ethyl 3-methylcyclohexane-6-one-1-carboxylate,

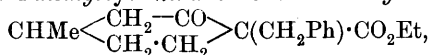


boils at 110° under 10 mm. pressure and forms a *semicarbazone*, $\text{C}_{11}\text{H}_{19}\text{O}_3\text{N}_3$, melting at 134°. *Ethyl 3-methyl-1-isopropylcyclohexane-6-one-1-carboxylate*, $\text{CH}_2 \begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CO} \end{array} \text{CPr}^\beta \cdot \text{CO}_2\text{Et}$, boils at 125—127°

under 10 mm. pressure and forms a *semicarbazone*, $\text{C}_{14}\text{H}_{25}\text{O}_3\text{N}_3$, melting at 130°. *m-Menthane-4-one*, $\text{CH}_2 \begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CO} \end{array} \text{CHPr}^\beta$, boils at 195°, has a sp. gr. 0·8914 at 15°, and forms an *oxime*, $\text{C}_{10}\text{H}_{19}\text{ON}$, melting at 105°. G. Y.

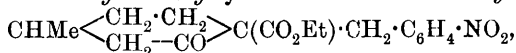
Syntheses by means of the Carboxylic Esters of Cyclic Ketones. III. Dicyclic Systems of indirectly connected Six-atom Rings. ARTHUR KÖTZ and GUSTAV KAYSER (*Annalen*, 1906, 348, 97—110. Compare Kötz and Hesse, this vol., i, 88; Kötz and Michels, preceding abstract).—The substances described in this paper were prepared by the action of the haloid compounds mentioned and sodium ethoxide on ethyl 4-methylcyclohexane-2-one-1-carboxylate in absolute alcoholic solution.

Ethyl 1-benzyl-4-methylcyclohexane-2-one-1-carboxylate,



from benzyl chloride, distils at 194° under 12 mm. pressure. The *semicarbazone*, $\text{C}_{18}\text{H}_{25}\text{O}_3\text{N}_3$, melts at 169°. When boiled with methylalcoholic potassium hydroxide, the ester yields 4-benzyl-1-methylcyclohexane-3-one, $\text{C}_6\text{H}_8\text{OMe} \cdot \text{CH}_2\text{Ph}$, which is colourless and boils at 166° under 10 mm. or at 173° under 13 mm. pressure; the *semicarbazone*, $\text{C}_{15}\text{H}_{21}\text{ON}_3$, melts at 172°; the *oxime*, $\text{C}_{14}\text{H}_{19}\text{ON}$, melts at 139°.

Ethyl 1-p-nitrobenzyl-4-methylcyclohexane-2-one-1-carboxylate,



from *p* nitrobenzyl chloride, crystallises in glistening, golden-yellow needles and melts at 90·5°.

The action of phenacyl bromide on ethyl 4-methylcyclohexane-2-one-1-carboxylate and sodium ethoxide leads to the formation of bromodiphenacyl.

Ethyl βκ-dimethylundecane-αηλ-tetracarboxylate,

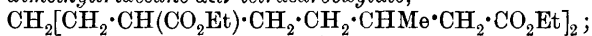


formed from methylene iodide, is obtained as a viscid oil boiling at 253° under 16 mm. pressure.

Only a small amount of ethyl β-methylpimelate is obtained from ethylene bromide, most of the ketone-ester being regained unchanged.

Ethyl 4 : 4'-dimethyl-1 : 1'-trimethylenedicyclohexane-2 : 2'-dione-1 : 1'-dicarboxylate, $\text{C}_3\text{H}_6(\text{C}_6\text{H}_7\text{OMe} \cdot \text{CO}_2\text{Et})_2$, formed from trimethylene dibromide, is obtained as a viscid oil which boils at 257—263° under

18 mm. pressure and is converted by the action of sodium ethoxide into ethyl $\beta\mu$ -dimethyltridecane- $\alpha\epsilon\iota$ -tetracarboxylate,



this forms a yellow oil boiling at $287\text{--}294^\circ$ under 14 mm. pressure. When boiled with methyl-alcoholic potassium hydroxide, the dicarboxylate is hydrolysed, and decomposes, forming 1:1'-dimethyl-4:4'-trimethylenedicyclohexane-3:3'-one; this forms a semicarbazone, $\text{C}_{19}\text{H}_{24}\text{O}_2\text{N}_6$, which melts at 107° and on treatment with sulphuric acid yields a small amount of a colourless oil boiling at about 204° . G. Y.

$\alpha\gamma$ -Diketocarboxylic Esters of the cyclopentane and Bicyclo-(O:1:3)-hexane Groups. ARTHUR KÖTZ, ARTHUR BIEBER, and P. SCHÜLER (*Annalen*, 1906, 348, 111—119).—Ethyl cyclopentane-

2-one-1-oxalate, $\begin{array}{c} \text{CH}_2-\text{CO} \\ | \\ \text{CH}_2\cdot\text{CH}_2 \end{array} > \text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$, prepared from cyclopentane-

2-one, ethyl oxalate, and sodium ethoxide in cooled absolute alcoholic solution, forms a colourless oil which boils at $138\text{--}139^\circ$ under 14 mm. pressure, gives a brown coloration with ferric chloride, and forms a semicarbazone. It resinifies when boiled under the ordinary pressure or when heated with dilute sulphuric acid, yields oxalic acid when boiled with dilute sodium hydroxide, and is partially decomposed at 150° in a sealed tube.

Ethyl 3:4-dimethyl-2-isopropylcyclopentene-5-one-1-oxalate (ethyl isothujoneoxalate), $\begin{array}{c} \text{CMe}-\text{CO} \\ | \\ \text{CMe}\cdot\text{CHPr}^\beta \end{array} > \text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$, prepared by acting with

sodium ethoxide on isothujone and ethyl oxalate in cooled absolute alcoholic solution, boils at $182\text{--}184^\circ$ under 11 mm. pressure, and when distilled under the ordinary pressure yields isothujone and a small amount of ethyl isothujonecarboxylate, $\text{C}_{13}\text{H}_{20}\text{O}_3$, which boils at 169° under 11 mm. pressure and gives a blue coloration with ferric chloride. The semicarbazone of ethyl isothujoneoxalate, $\text{C}_{15}\text{H}_{23}\text{O}_4\text{N}_3$, melts at $168\text{--}169^\circ$.

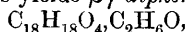
Ethyl thujoneoxalate, $\text{CH}_2 < \begin{array}{c} \text{CH} \\ | \\ \text{CPr}^\beta \end{array} \text{---} \text{CHMe} > \text{CO}$, formed in similar manner to the iso-ester, boils at $168\text{--}170^\circ$ under 11 mm. pressure; the semicarbazone, $\text{C}_{15}\text{H}_{23}\text{O}_4\text{N}_3$, melts at $156\text{--}157^\circ$. When boiled under the ordinary pressure for two days, the ester yields a mixture of thujone and ethyl thujonecarboxylate, $\text{C}_{13}\text{H}_{20}\text{O}_3$, which gives a violet coloration with ferric chloride. A similar mixture is obtained by heating the ethyl oxalate under pressure at 220° . On prolonged heating with dilute sulphuric acid, the ethyl oxalate yields oxalic acid, thujone, and isothujone, whilst with concentrated hydrochloric acid at 125° oxalic acid, carbon monoxide and dioxide, and isothujone are formed.

The behaviour, when heated under the ordinary pressure, of the product formed with sodium ethoxide and ethyl oxalate may be used to determine whether the group $-\text{CH}_2\cdot\text{CO}$ is present in a five- or six-atom ring. G. Y.

Benzoylsalicylic [*o*-Benzoyloxybenzoic] Acid. F. HOFFMANN, LA ROCHE & Co. (D.R.-P. 169247).—*o*-Benzoyloxybenzoic acid, $\text{OBz}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, and its salts have not hitherto been obtained, but the acid is prepared readily by treating disodium salicylate at low temperatures with 1 mol. or slight excess of benzoyl chloride diluted with petroleum or ether. The residue after pouring off the diluent is extracted with water and the *o*-benzoyloxybenzoic acid precipitated with acid and recrystallised from dilute alcohol. It is quite insoluble in cold water, dissolving sparingly on warming; it dissolves readily in ether, alcohol, or chloroform and does not give the reactions of salicylic acid until after hydrolysis with alkalis. The crystalline acid melts at 132° . G. T. M.

Reduction of $\alpha\beta$ -Unsaturated Carboxylic Esters with Aluminium Amalgam. FRANZ HENLE (*Annalen*, 1906, 348, 16—30. Compare Thiele and Buehner, this vol., i, 569; Harries and Eschenbach, *Abstr.*, 1896, i, 305; H. Wislicenus, *Abstr.*, 1896, i, 672).—Methyl cinnamate is reduced by aluminium amalgam and water in ethereal solution in four to six days, forming methyl dihydrocinnamate in a yield of 55—65 per cent., methyl $\beta\gamma$ -diphenyladipate in a yield of 8—9 per cent., and an isomeride of the latter melting at 73° in a yield of 4—5 per cent.

Methyl $\beta\gamma$ -diphenyladipate, $\text{CO}_2\text{Me}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$, crystallises from ethyl acetate, melts at 175° , is sparingly soluble in hot ether, alcohol, or light petroleum, but readily so in other hot organic solvents, does not decolorise potassium permanganate or bromine, and on hydrolysis yields *$\beta\gamma$ -diphenyladipic acid*,

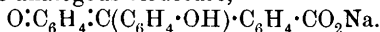


which crystallises from alcohol in small, glistening, colourless prisms, loses $\text{C}_2\text{H}_6\text{O}$ at 105° , melts at about 270° , is insoluble in water, reddens moist litmus paper in alcoholic solution, and dissolves in aqueous sodium carbonate. When fused with potassium hydroxide, the acid is oxidised, forming benzoic and acetic acids. *$\beta\gamma$ -Diphenyladipic diacetic anhydride*, $\text{C}_4\text{H}_6\text{Ph}_2(\text{CO}\cdot\text{OAc})_2$, formed by boiling the acid with acetyl chloride in a reflux apparatus, crystallises from light petroleum, melts at 100 — 105° , resolidifies on further heating, and melts again to a yellow liquid at 235 — 240° . It is soluble in chloroform, loses acetic anhydride slowly in a vacuum, quickly at 140° , forming a brown, granular mass, which is not the adipic anhydride, melts at 225 — 240° , and is soluble in boiling nitrobenzene. The mixed anhydride is hydrolysed by boiling water, forming acetic and *$\beta\gamma$ -diphenyladipic acids*. A white substance, only sparingly soluble in chloroform and insoluble in aqueous sodium carbonate, is formed together with the mixed anhydride by the action of freshly-distilled acetyl chloride on *$\beta\gamma$ -diphenyladipic acid*.

The isomeride of methyl *$\beta\gamma$ -diphenyladipate*, $\text{C}_{20}\text{H}_{22}\text{O}_4$, melting at 73° , crystallises from hot light petroleum, is readily soluble in other organic solvents, and behaves as a saturated ester towards potassium permanganate and bromine. The acid, $\text{C}_{18}\text{H}_{18}\text{O}_4$, crystallises from water, melts at 169 — 170° , has an acid reaction in aqueous solution, and is probably a stereoisomeride of the *$\beta\gamma$ -diphenyladipic acid* melting at 270° .

Ethyl benzylmalonate is obtained in a 60 per cent. yield by the reduction of ethyl benzylidenemalonate with aluminium amalgam and moist ether. Ethyl cinnamylidenemalonate also is reduced by aluminium amalgam and moist ether. G. Y.

Constitution of the Phenolphthalein and Quinolpthalein Salts. ARTHUR G. GREEN and PERCY E. KING (*Ber.*, 1906, **39**, 2365—2371).—A reply to Meyer and Spengler's criticism (*Abstr.*, 1905, i, 440) of the views of Green and Perkin (*Trans.*, 1904, **85**, 398). The following facts prove the existence of coloured quinonoid alkyl esters of the phthaleins, such as $O:C_6H_4:C(C_6H_4\cdot OH)\cdot C_6H_4\cdot CO_2Me$, and hence support the contention that the coloured alkali salts of the phthaleins have the analogous structure,



The analogy between the phthaleins and the fluoresceins, assumed in the previous paper, is thus made complete; the apparent differences between the two series are in reality merely differences of stability.

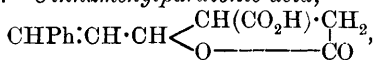
The ester, $O:C_6H_4:C(C_6H_4\cdot OH)\cdot C_6H_4\cdot CO_2Me$, prepared by saturating a methyl-alcoholic solution of phenolphthalein containing zinc chloride with hydrogen chloride, and subsequently pouring the solution into ice-cold water, forms a scarlet-red precipitate, which is rapidly hydrolysed by water at the ordinary temperature, becoming colourless; even when dried in a desiccator, partial hydrolysis takes place, the colour changing from dark red to rose-red. The same red salt is apparently formed on heating phenolphthalein with methyl sulphate, giving a red solution, but it has not yet been isolated.

On passing hydrogen chloride through a solution of quinolphthalein in methyl alcohol, small, red crystals of the *chloride* of the *quinonoid methyl ester*, $CO_2Me\cdot C_6H_4\cdot C\begin{smallmatrix} \swarrow C_6H_3(OH) \\ \searrow C_6H_3(OH) \end{smallmatrix}O\cdot Cl$, separate; this substance is stable when dry and is much less easily decomposed by water than the quinonoid ester of phenolphthalein. When heated with aqueous alkalis it is, however, rapidly converted into the ordinary violet salts of quinolphthalein.

The *chloride*, $CO_2H\cdot C_6H_4\cdot C\begin{smallmatrix} \swarrow C_6H_3(OH) \\ \searrow C_6H_3(OH) \end{smallmatrix}O\cdot Cl$, of quinolphthalein, prepared by passing hydrogen chloride into a warm solution of the phthalein in glacial acetic acid, also forms red crystals; it is decomposed instantaneously by water, alcohol, or by ether containing alcohol.

W. A. D.

Cinnamenylparaconic Acid. J. BOUGAULT (*Compt. rend.*, 1906, **142**, 1539—1541).—*Cinnamenylparaconic acid*,



prepared by the action of cinnamaldehyde on sodium succinate in the presence of acetic anhydride, melts at 145° , is very sparingly soluble in water, benzene, or light petroleum, sparingly soluble in ether or chloroform, a little more so in cold alcohol (0.5 to 0.6 per cent.), much more soluble in hot alcohol; it is reprecipitated immediately by a

strong acid from solution in sodium carbonate, but only after several hours from solution in sodium hydroxide; the *dibromide* is crystalline, and melts and decomposes at 205° ; it is very sparingly soluble in the ordinary solvents, dissolves readily in sodium carbonate, but when the solution is heated decomposition ensues with the formation of sodium bromide, benzaldehyde, and other products not yet examined.

Cinnamenylparaconic acid is readily converted by the action of boiling water into cinnamenylisocrotonic acid, which was the only product obtained by Fittig and Batt (Abstr., 1904, i, 744), who first examined the action of cinnamaldehyde on sodium succinate. M. A. W.

Salts of Mineral Acids derived from the Phthaleins. I. GUSTAV HELLER [and, in part, OTTO LANGKOPF] (*Zeit. Farb. Ind.*, 1906, 5, 265—269).—*Gallein hydrochloride alcoholate*, $C_{20}H_{12}O_7 \cdot HCl \cdot C_2H_6O$, prepared by dissolving gallein in alcoholic hydrochloric acid, crystallises in brown prisms or plates. The corresponding *acetone* derivative, $C_{20}H_{12}O_7 \cdot HCl \cdot C_3H_6O$, obtained from gallein, hydrochloric acid, and acetone, forms bluish-black needles. The formation of these substances can be utilised in purifying gallein. Pure gallein, obtained by decomposing either of the above compounds with concentrated sulphuric acid and adding water to the filtered solution, differs from ordinary gallein by giving only a slight yellowish-red coloration when dissolved in alcohol or acetone. *Gallein hydrochloride methyl alcoholate*, $C_{20}H_{12}O_7 \cdot HCl \cdot MeOH$, crystallises from methyl alcohol on adding ether in clusters of needles. *Gallein sulphate*, $C_{20}H_{12}O_7 \cdot H_2SO_4$, does not crystallise with alcohol or acetone. The *hydrobromide*, however, like the hydrochloride, crystallises from acetone with 1 mol. of the solvent.

Gallein ethyl ester gives with hydrochloric acid in presence of either alcohol or acetone the *hydrochloride*, $C_{22}H_{16}O_7 \cdot HCl$, which forms brownish-red needles and does not crystallise with the solvent. The analogous *sulphate*, $C_{22}H_{16}O_7 \cdot H_2SO_4$, is similar.

All the foregoing salts of gallein are decomposed by cold water. On adding an alcoholic solution of any one of them to boiling water, the reddish-brown *gallein hydrate*, $C_{20}H_{12}O_7 \cdot H_2O$, separates as a crystalline powder which loses $1H_2O$ at 180° . A second modification of this substance, having a bluish-violet colour when dried in a vacuum, is obtained by adding the alcoholic solution of the salt to cold water, or by decomposing by a mineral acid the salts formed by gallein with alkalis. A third hydrated form is obtained as a blackish-red, crystalline powder on adding chloroform to a solution of pure gallein in acetone or by decomposing an alkali salt of gallein with acetic acid. Anhydrous gallein, obtained by expelling water from the hydrated forms or by fusing phthalic anhydride with pyrogallol, forms nearly black crystals. The relationship between the foregoing substances will be discussed in a subsequent paper. The alkali salts of gallein also exist in two modifications. The salt obtained by dissolving gallein in alkali is intensely violet; a red *potassium* salt, $C_{20}H_{11}O_7 \cdot K$, is, however, formed on mixing alcoholic solutions of gallein and of potassium acetate.

Hydroxyquinolphthalein (Feuerstein and Dutoit, Abstr., 1901, i, 723) gives salts similar to those of gallein; the *hydrochloride ethyl*

alcoholate, *methyl alcoholate*, and *acetate* are described. The *sulphate*, $C_{20}H_{12}O_7 \cdot H_2SO_4$, does not crystallise with the solvent.

Coerulein hydrochloride and *sulphate* were prepared; these salts contain only about three-fourths of the amount of acid calculated for the formulæ $C_{20}H_{10}O_6 \cdot HCl$ and $C_{20}H_{10}O_6 \cdot H_2SO_4$ respectively. W. A. D.

Compounds from Lichens. XV. WILHELM ZOPF (*Annalen*, 1906, 346, 82—127. Compare *Abstr.*, 1905, i, 212, 789).—The lichen, *Rhizoplaca chryssoleuca*, Zopf (*Lecanora chryssoleuca*, Ach; *Squamaria chryssoleuca*, or *Placodium chryssoleucum*), contains usnic acid and placodiolin, or, better, *placodiolic acid*, $C_{17}H_{18}O_7$, the latter of which dissolves when the plant is extracted with sodium hydrogen carbonate. It is precipitated from the solution with acid, and crystallises in leaflets or monoclinic, yellowish-green plates, melting at $156—157^\circ$; in chloroform solution it has $[\alpha]_D - 238^\circ$ at 17° ; its mol. weight was determined in acetone and cryoscopically in benzene, and found to be 315.6 in the one and 306 in the other solvent. In alkaline solution, the acid reduces potassium permanganate.

The usnic acid obtained from *Rhizoplaca opaca*, Zopf, has $[\alpha]_D - 482.3^\circ$ at 22° , and was converted into Widman's decarbousnic acid melting at 176° .

Contrary to previous statements, neither zeorin nor sordidin was found in *Lecanora sulphurea*, but a crystalline substance melting at 100° was found together with usnic acid. It would appear that two modifications of this lichen exist, distinct in their chemical characters.

It is suggested that the rhizocarpinic acid melting at 170° described by Hesse is impure rhizocarpic acid which melts at $177—179^\circ$.

Biatora Lightfootii contains at least 6 per cent. of *l*-usnic acid ($[\alpha]_D - 455.9^\circ$), to which is ascribed the yellowish- or greyish-green colour of the thallus. A colourless, crystalline compound is also present in small quantities.

The lichen, *Biatora granulosa* (*Lecidea granulosa* var. *decolorans*, *Patellaria decolorans*), contains gyrophoric acid melting at $202—203^\circ$, which, when heated with alcohol in a closed tube, yields ethyl orsellate melting at 132° . The presence of paretin is probably the cause of the violet colour which extracts of *Blastenia Jungermanniae* give with alkali hydroxides.

Diploschistessic acid, $C_{15}H_{16}O_7$, is present to the extent of 2—3 per cent., together with atranoric acid, in *Diploschistes scruposus* (*Patellaria scruposa* or *Urceolaria scruposa*); it crystallises in short needles or rosettes of leaflets melting at $164—165^\circ$; its mol. weight was determined in acetone solution; it dissolves in alkali hydroxides to a yellow solution; its alcoholic solution is coloured violet by ferric chloride, and with bleaching powder it gives first a red, then a violet, and finally an indigo coloration. It is converted by acetic acid into orsellic acid, by alcohol into ethyl orsellate; it immediately reduces potassium permanganate, and is changed by potassium hydroxide into a substance resembling orcinol. From these characters it is concluded that this acid is a derivative of orsellic acid, but different from patellic acid and other orsellic acid derivatives. It is suggested that the acid described by Hesse as lecanoric acid in *Urceolaria bryophila* is impure

diploschistessic acid. *Cladina rangiferina* contains, together with atranoric acid, fumarprotocetraric acid and not cetraric acid. In *Cladina destrieta* the presence of destrietic acid cannot be affirmed, although a colourless compound is present together with *l*-usnic acid.

Cladina silvatica (*Cladonia rangiferina* var. *silvatica*) contains *d*-usnic acid ($[\alpha]_D + 491.4^\circ$ in chloroform solution at 22°), and thus differs from other *Cladoniaceæ*; the cetrarin also present is probably fumarprotocetraric acid.

The lichen, *Cladina silvatica* var. *spumosa* (*Cladonia rangiferina* var. *spumosa* or *Cladonia silvatica* var. *sylvestris*) cannot be regarded, as hitherto, simply as a variety of *Cladina silvatica*, since it contains 0.7 per cent. of *l*-usnic acid ($[\alpha]_D - 490.8^\circ$ at 17° in chloroform solution). It is rather to be regarded as a variety of *Cladina alpestris*, and named *Cl. alpestris* var. *spumosa*.

Leiphæmin, which is found in *Hæmatomma leiphæmum*, forms rhombic crystals. In the lichen, *Hæmatomma porphyrium*, $\frac{1}{2}$ per cent. of atranoric acid, 1 per cent. of zeorin, 1 per cent. of porphyrylic acid, 1 per cent. of leiphæmin, and a small amount of hymenorrhodin are found. The last mentioned crystallises in rhombic, red plates and gives purple or violet colorations with alkalis and sulphuric acid; it would thus appear to be an anthracene derivative. These facts show that the view that *Hæmatomma porphyrium* and *H. leiphæmum* are identical is untenable. *Hæmatomma coccineum* (*Hæmatomma coccineum* var. *ochroleucum* or *Lecanora hæmatomma coccinea*) contains *l*-usnic acid $2\frac{1}{2}$, zeorin $\frac{1}{2}$, atranoric acid about $\frac{1}{3}$, porphyrylic acid 2, and leiphæmin 2 per cent., also a very small quantity of hymenorrhodin; Hesse's hæmatommidin is probably identical with leiphæmin.

Parmelia Mougeotti contains *d*-usnic acid.

Lepraria candelaris contains 20—22 per cent. of calycin; the presence of pinastric acid was not established. *Cyphelium trichiale* var. *candelare* contains 8 per cent. of calycin. K. J. P. O.

***o*-Nitrobenzophenone and its Reduction Products.** CARLO BÆZNER and AUGUST GARDIOL (*Ber.*, 1906, 39, 2512—2514).—

Phenyldihydroanthranil, $C_6H_4 \begin{smallmatrix} \text{CHPh} \\ \text{NH} \end{smallmatrix} O$, is prepared by reduction of *o*-nitrobenzophenone with aluminium amalgam in ethereal solution, or electrolytically in aqueous-alcoholic sodium acetate solution, with a lead cathode and a lead anode in cold saturated aqueous sodium carbonate; it forms glistening, pale yellow crystals and melts at 116.5° . G. Y.

Observations in the Diphenylmethane and Xanthone Series. OTTO DIELS and KARL ROSENMUND (*Ber.*, 1906, 39, 2358—2364).—

The substance formerly described as 5:5'-dibromo-2-hydroxy-2'-ethoxybenzophenone, $CH \begin{smallmatrix} \text{CH} \cdot \text{C}(\text{OH}) \\ \text{CBr} = \text{CH} \end{smallmatrix} \text{C} \cdot \text{CO} \cdot \text{C} \begin{smallmatrix} \text{C}(\text{OEt}) \cdot \text{CH} \\ \text{CH} = \text{CBr} \end{smallmatrix} CH$ (*Abstr.*, 1905, i, 432), is shown by the following facts to have this structure, and not that of an alcoholate of 2:7-dibromoxanthone, as might be supposed from the ease with which it is converted into the latter substance. The reason for its instability is discussed at length.

With phenylhydrazine, the substance gives the *phenylhydrazone*, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{C}(\text{N}_2\text{HPh})\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{OEt}$, which crystallises from alcohol in yellow needles and melts at 165° . The *oxime*,

$\text{OH}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{C}(\text{:NOH})\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{OEt}$, crystallises from chloroform and melts at $181\text{--}182^\circ$. The *acetyl* derivative, $\text{OAc}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CO}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{OEt}$, is easily obtained by direct acetylation, crystallises from alcohol in needles, and melts at $105\text{--}107^\circ$.

The monoethyl ether is easily reconverted into the diethyl ether, $\text{CO}(\text{C}_6\text{H}_3\text{Br}\cdot\text{OEt})_2$, by treating it with potassium in benzene solution and heating the product with ethyl iodide. The ease, however, with which it is converted into 2:7-dibromoxanthone is shown by the fact that this substance begins to separate almost immediately on heating with *N*/20 potassium hydroxide.

5:5'-Dibromo-2:2'-dimethoxydiphenylmethane, $\text{CH}_2(\text{C}_6\text{H}_3\text{Br}\cdot\text{OMe})_2$, prepared by adding 20 per cent. formaldehyde to a solution of *p*-bromoanisole in dilute sulphuric acid at -10° , crystallises from alcohol and melts at 108° . On oxidation with chromic acid in glacial acetic acid solution, it gives 5:5'-dibromo-2:2'-dimethoxybenzophenone,

$\text{CO}(\text{C}_6\text{H}_3\text{Br}\cdot\text{OMe})_2$, which crystallises from alcohol or glacial acetic acid and melts at 123° ; on heating this with concentrated hydrochloric acid for five hours at 160° , 5:5'-dibromo-2-hydroxy-2'-methoxybenzophenone,

$\text{OH}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CO}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{OMe}$, is obtained. The latter crystallises from alcohol in deep yellow needles, melts at 159° , and differs from the analogous ethoxy-derivative in giving 5:5'-dibromo-2:2'-dihydroxybenzophenone,

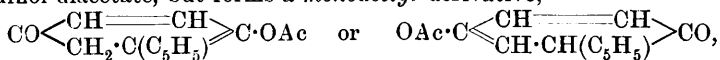
$\text{CO}(\text{C}_6\text{H}_3\text{Br}\cdot\text{OH})_2$, when it is heated with aluminium chloride and the product decomposed by water; the dihydroxy-compound crystallises from light petroleum in yellow leaflets, melts at $138\cdot5^\circ$, and differs from its monomethyl and monoethyl ethers by not being convertible into dibromoxanthone by concentrated acids or alkalis, or by phosphoric oxide or zinc chloride. With diazomethane, however, yellow needles melting at 156° are obtained, which, on heating with alkali, readily give the 2:7-dibromoxanthone. W. A. D.

Hydrobenzoin. AUGUST KLAGES (*Ber.*, 1906, 39, 2356—2357).—The product obtained by treating benzoin according to Apitzsch and Metzger's method (*Abstr.*, 1904, i, 510) is not hydrobenzoin, but unchanged benzoin; its true nature is shown by the properties of its derivatives. Apitzsch and Metzger were probably led into error owing to the melting point of hydrobenzoin being identical with that of benzoin. W. A. D.

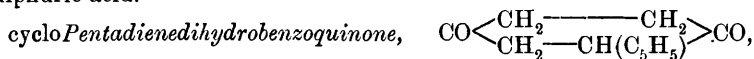
Additive Products of cyclopentadiene and Quinones. WALTHER ALBRECHT (*Annalen*, 1906, 348, 31—49).—With 1—2 mols. of cyclopentadiene, benzoquinone forms *additive* compounds, to which no satisfactory constitutions can be ascribed; those given are in accordance with most of the properties of the substances, but not with the reduction of cyclopentadienequinone to a dihydro-derivative which is

not a quinol, nor with the stability of the chloranil derivative of *cyclopentadiene*.

cyclopentadienebenzoquinone, $\text{CH} \begin{smallmatrix} \text{CH} - \text{CO} \\ \text{CO} - \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{C}_5\text{H}_5$, formed with development of heat by the action of 1 mol. of *cyclopentadiene* on 1 mol. of benzoquinone in cooled alcoholic solution, crystallises in long, slender, slightly yellow needles, or flat, greenish-yellow prisms, melts at 77—78°, decomposes into its generators when more highly heated, is readily soluble in organic solvents, and gives in alkaline solution a deep red to yellow, in concentrated sulphuric acid a red coloration, and a blue, flocculent precipitate on addition of water. It forms an intense blue solution when heated with zinc chloride and glacial acetic acid, reduces ammoniacal silver nitrate at the ordinary temperature and Fehling's solution on boiling, forms an unstable *dibromide*, and gives precipitates with hydroxylamine and phenylhydrazine. When evaporated with acetic anhydride, *cyclopentadienebenzoquinone* yields quinol diacetate, but forms a *monoacetyl* derivative,



when treated with acetic anhydride and cooled concentrated sulphuric acid; this crystallises in white needles, melts at 91—92°, gives a blue coloration with glacial acetic and concentrated sulphuric acids, and yields benzoquinone when boiled with ferric chloride solution. The *semicarbazone* of *cyclopentadienebenzoquinone*, $\text{C}_{13}\text{H}_{16}\text{O}_2\text{N}_6$ or $\text{C}_{13}\text{H}_{18}\text{O}_3\text{N}_6$, forms a fine, white powder, decomposes at about 220°, and gives an intense yellow coloration with concentrated sulphuric acid.

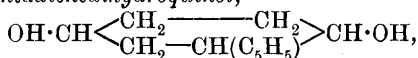


formed by reduction of *cyclopentadienebenzoquinone* by zinc dust in glacial acetic acid solution, separates from alcohol in white crystals, melts at 34—35°, decomposes when distilled, forming *cyclopentadiene* and quinol, is soluble in the usual solvents, gives a reddish-violet coloration with concentrated sulphuric acid, reduces ammoniacal silver nitrate and Fehling's solutions at the ordinary temperature, and is converted by concentrated potassium hydroxide into an insoluble, white *polymeride*, $(\text{C}_{11}\text{H}_{12}\text{O}_2)_x$, melting above 270°. The dihydrodiketone forms a yellow *precipitate* with phenylhydrazine in aqueous solution, a *semicarbazone* melting at 222—224°, and with Baeyer's reagent a *ferrocyanide* crystallising in long, colourless needles. The *dioxime*, $\text{C}_{11}\text{H}_{14}\text{O}_2\text{N}_2$, crystallises in white needles and decomposes at 188°. With bromine in ethereal solution, the dihydrodiketone forms a *hydroxybromide*, $\text{C}_{11}\text{H}_{12}\text{O}_2\text{Br} \cdot \text{OH}$, which crystallises in colourless prisms, melts at 132—133°, absorbs 1 mol. of bromine in chloroform solution, and when boiled with a copper-zinc couple and acetic acid in alcoholic solution yields the dihydrodiketone. The *dibromide*, $\text{C}_{11}\text{H}_{12}\text{O}_2\text{Br}_2$, is formed in slender needles by the action of hydrogen bromide on the hydroxybromide in chloroform solution and melts at 138—139°. The action of methyl-alcoholic potassium hydroxide on the hydroxybromide leads to the formation of the *oxide*, $\text{C}_{11}\text{H}_{12}\text{O}_3$, which crystallises in small prisms, melts at 149—150°, and re-forms

the hydroxybromide when treated with hydrogen bromide in glacial acetic acid solution.

The *pinacone*, $C_{22}H_{22}O_4$, formed together with the dihydrodiketone by the reduction of *cyclopentadienebenzoquinone* with zinc dust, crystallises in white leaflets, melts at $188-189^\circ$, gives a reddish-violet coloration with concentrated sulphuric acid, reduces ammoniacal silver nitrate on boiling, or dilute potassium permanganate at the ordinary temperature, and forms a deep red, sparingly soluble *product* with phenylhydrazine.

trans-cyclopentadienedihydroquinol,



prepared together with a yellow oil, $C_{11}H_{16}O_2, \frac{1}{2}H_2O$, which is probably the *cis-form*, by reduction of dihydro*cyclopentadienebenzoquinone* with sodium amalgam, crystallises in stellate aggregates of needles, melts at 88° , and on exposure to air absorbs $\frac{1}{2}H_2O$, forming dull crystals melting at $96-98^\circ$. The *dibenzoate*, $C_{25}H_{24}O_4$, crystallises in slender needles and melts at $166-167^\circ$.

With chloranil, *cyclopentadiene* reacts in benzene solution in presence of trimethylamine, forming the *additive* compound, $C_{11}H_6O_2Cl_4$, which crystallises from absolute alcohol in long, strongly refracting, yellow needles, melts at $146-146.5^\circ$, gives with concentrated sulphuric acid a violet, with alcoholic potassium hydroxide a yellowish-red solution, reduces ammoniacal silver nitrate on boiling, reacts violently with phenylhydrazine, and with bromine in chloroform solution in direct sunlight forms a *dibromide*, $C_{11}H_6O_2Cl_4Br_2$, crystallising in glistening, white leaflets and melting at 269° .

cyclopentadiene- α -naphthaquinone, $C_{15}H_{12}O_2$, prepared from *cyclopentadiene* and α -naphthaquinone in benzene solution, crystallises in slender, white prisms, melts at $115-116^\circ$, reduces ammoniacal silver and Fehling's solutions at the ordinary temperature, gives a red coloration with alkali hydroxides or concentrated sulphuric acid, and forms *precipitates* with phenylhydrazine and semicarbazide acetates.

Dicyclopentadienebenzoquinone, $CO < \begin{array}{c} CH_2 \cdot CH(C_5H_5) \\ CH(C_5H_5) \cdot CH_2 \end{array} > CO$, formed by the action of 2 mols. of *cyclopentadiene* on 1 mol. of benzoquinone in benzene or alcoholic solution, crystallises in glistening, white leaflets or needles, melts at $157-158^\circ$, is soluble in organic solvents, only slightly volatile in a current of steam, is insoluble in aqueous alkali hydroxides, reduces ammoniacal silver and Fehling's solutions on boiling, behaves in the same manner as *cyclopentadienebenzoquinone* towards concentrated sulphuric acid and zinc and ferric chlorides, and forms a red *oil* with phenylhydrazine and an insoluble white *disemicarbazone*, melting above 270° . The *dioxime*, $C_{16}H_{18}O_2N_2$, crystallises from alcohol, becomes brown at 185° , and does not melt at 270° . With bromine in chloroform solution, *dicyclopentadienebenzoquinone* forms a *dibromide* which, on recrystallisation from alcohol, yields the *ethoxybromide*, $C_{18}H_{21}O_3Br$, crystallising in slender, white needles and melting at 142° . The *methoxybromide*, $C_{17}H_{19}O_3Br$, crystallises in slender, white needles and melts at 188° .

cyclopentadiene does not react with anthraquinone, phenanthra-

quinone, β -naphthaquinone, benzil, benzylideneacetone, phorone, or dibenzoylstyrene. G. Y.

Anthraquinone- α -sulphonic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 167169).— α -Nitroalizarin and α -nitroanthraquinonesulphonic acids behave like α -nitroanthraquinone on treatment with hot aqueous alkali sulphites, the α -nitro-group being replaced by a sulpho-group.

α -Nitroalizarin and α -nitroanthraquinone-6-sulphonic acid, when treated in this way, give rise to alizarin- α -sulphonic and anthraquinone-1 : 6-disulphonic acids respectively. The α -nitroanthraquinonesulphonic acids, containing their sulphonic groups in positions 5, 7, and 8, behave in a similar manner. G. T. M.

Preparation of Anthraquinone-di- and -tri-sulphonic Acids. R. WEDEKIND & Co. (D.R.-P. 170329).—Potassium anthraquinone- α -sulphonate, when sulphonated with fuming sulphuric acid in the presence of mercury, yields anthraquinone-1 : 5- and -1 : 8-disulphonic acids. In the absence of mercury, the sulphonation leads to the production of the 1 : 7- and 1 : 6-disulphonic acids and a trisulphonic acid of unknown constitution. On heating this mixture of acids under pressure with milk of lime containing calcium chloride and potassium nitrate, 1 : 7- and 1 : 6-dihydroxyanthraquinones are produced, together with about 25 per cent. of a new *dihydroxyanthraquinonesulphonic acid*, the *barium* salt, $C_{28}H_{14}O_{14}S_2Ba$, of which crystallises from hot water in orange needles. G. T. M.

Preparation of the Carbamates of the Nitroaminoanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 167410).—*o*-Nitro-derivatives of the aminoanthraquinones cannot be prepared either from the aminoanthraquinones themselves or from their acyl derivatives. In the former case, the nitration does not proceed smoothly, and in the latter only *p*-nitro-derivatives are produced. Nitration of the carbamates of the aminoanthraquinones, however, leads to the production of the important *o*-nitroamino-derivatives. The *carbamate* of β -aminoanthraquinone, obtained by heating together β -aminoanthraquinone and ethyl chlorocarbonate in nitrobenzene solution, separates on cooling in golden-yellow leaflets; on nitration with a mixture of concentrated nitric and sulphuric acids, it yields 1-nitro-2-aminoanthraquinone and 3-nitro-2-aminoanthraquinone, these isomerides being separated by crystallisation from nitrobenzene, in which the latter is the less soluble. Similarly, the carbamate of α -aminoanthraquinone furnishes a mixture of the ortho- and para-nitro-compounds, which are also separated by means of nitrobenzene, in which the para-isomeride is the less soluble. G. T. M.

Preparation of α -Nitro- β -methoxyanthraquinones. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 167699).—The energetic nitration of anthraquinone in concentrated sulphuric acid solution gives rise to the 1 : 5- and 1 : 8-dinitroanthraquinones as chief products, but 40 per cent. of the nitrated material consists of a

mixture of other isomerides which have been separated by fractional crystallisation from nitrobenzene and other solvents and characterised by conversion into dimethoxyanthraquinones and dihydroxyanthraquinones successively.

The $\beta\beta$ -dinitroanthraquinones are present only in very small quantities in the product of nitration. The $\alpha\beta$ -isomerides, of which the 1 : 6-compound is formed in largest amount, behave differently from the $\alpha\alpha$ -compounds towards sodium methoxide. In the $\alpha\beta$ -series, the β -nitro-group is readily replaced by methoxyl, and an α -nitro- β -methoxyanthraquinone results; the $\alpha\alpha$ -compounds are attacked only with great difficulty, and then both nitro-groups are replaced by methoxyl.

1-Nitro-6-methoxyanthraquinone is readily formed by heating together 1 : 6-dinitroanthraquinone and sodium methoxide in methyl alcohol; it crystallises from benzene in lustrous, yellow leaflets melting at 268° . With concentrated sulphuric acid, the methoxy-derivative develops an orange colour; it dissolves in aqueous sodium sulphide to a pale bluish-green solution, from which, on warming, 1-amino-6-methoxyanthraquinone separates as an orange-yellow precipitate.

1-Nitro-7-methoxyanthraquinone crystallises from benzene in slightly coloured needles melting at 238° ; on reduction with sodium sulphide, it furnishes the orange-red 1-amino-7-methoxyanthraquinone.

These methoxy-derivatives are readily hydrolysed to α -nitro- β -hydroxyanthraquinones by concentrated hydrochloric and acetic acids. The α -amino- β -hydroxyanthraquinones may be obtained either by reducing the α -nitro- β -hydroxy-derivatives or by hydrolysing the α -amino- β -methoxy-derivatives.

The patent contains a table of the properties of the dinitro- and dimethoxy-anthraquinones.

G. T. M.

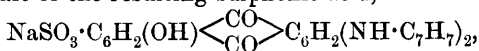
A New Derivative of Anthraquinone. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 167461).—Although the fusion of erythrohydroxyanthraquinone with potassium hydroxide furnishes a certain amount of alizarin, yet the main product of this reaction is a substance, $C_{28}H_{14}O_6$, hitherto uncharacterised, which, in view of its sparing solubility, is probably formed by the condensation of 2 molecules of erythrohydroxyanthraquinone; the alkali salts of this compound, which are also very insoluble, point to its being a hydroxy-derivative. It crystallises from diphenylmethylamine in golden-yellow needles, and yields with alkaline solutions of sodium hyposulphite a leuco-derivative which is somewhat more soluble in aqueous alkali.

G. T. M.

Preparation of *p*-Mono- and *p*-Di-chloroanthrarufin. R. WEDEKIND & Co. (D.R.-P. 167743).—Hitherto anthrarufin has only been successfully chlorinated when suspended or dissolved in glacial acetic acid. It is now found that when suspended in dilute sulphuric acid boiling at 140° and treated slowly with the calculated amount of potassium chlorate and sodium chloride in aqueous solution, anthrarufin may be quantitatively converted into either *p*-mono- or *p*-chloro-anthrarufin.

G. T. M.

[**Sulphonation of α -Hydroxyquinizarin-green.**] FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 170113).— α -Hydroxyquinizarin-green, $\text{HO}\cdot\text{C}_6\text{H}_3\langle\begin{smallmatrix}\text{CO} \\ \text{CO}\end{smallmatrix}\rangle\text{C}_6\text{H}_2(\text{NH}\cdot\text{C}_7\text{H}_7)_2$, when sulphonated in the usual way, yields mono- and di-sulphonic derivatives containing the sulpho-groups in the toluene nuclei. When, however, the sulphonation is effected by fuming sulphuric acid in the presence of boric acid, the sulpho-groups enter the anthraquinone residue exclusively. The sodium salt of the resulting sulphonic acid,



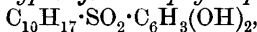
is sparingly soluble in hot water, but dissolves more readily in dilute acetic acid. Its colour in concentrated sulphuric acid is violet-blue, whereas the other sulphonic acids of α -hydroxyquinizarin-green develop greenish-blue or bluish-green colorations. G. T. M.

Thioborneol and other Derivatives of Camphane containing Sulphur. WALTHER BORSCHKE and W. LANGE (*Ber.*, 1906,

39, 2346—2356).—*Camphane-2-sulphinic acid*, $\begin{array}{c} \text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{SO}_2\text{H} \\ | \\ \text{CMe}_2 \\ | \\ \text{CH}_2\cdot\text{CH}\cdot\text{CH}_2 \end{array}$,

prepared by saturating an ice-cold ethereal solution of magnesium camphyl chloride with sulphur dioxide, forms a colourless syrup, which is only sparingly soluble in water; when cooled in a mixture of ice and salt, it gelatinises, but does not crystallise. The *sodium salt*, $\text{C}_{10}\text{H}_{17}\cdot\text{SO}_2\text{Na}$, crystallises from water.

Methylcamphylsulphone, $\text{C}_{10}\text{H}_{17}\cdot\text{SO}_2\text{Me}$, prepared by warming the sulphinic acid with alcoholic sodium ethoxide and methyl iodide, crystallises from dilute alcohol in long, slender needles and melts at 57—58°. 1:4-*Dihydroxyphenyl-2-camphylsulphone*,



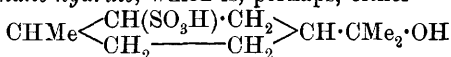
prepared by the action of the sulphinic acid on benzoquinone, separates from benzene or glacial acetic acid in colourless crystals and melts at 186—187°.

Camphane-2-sulphonic bromide, $\text{C}_{10}\text{H}_{17}\cdot\text{SO}_2\text{Br}$, prepared by the action of bromine at 0° on camphylsulphinic acid dissolved in aqueous potassium hydroxide, forms a nearly colourless oil, which, with ammonia, gives *camphane-2-sulphonamide*; this crystallises from a mixture of benzene and light petroleum and melts at 122—123°.

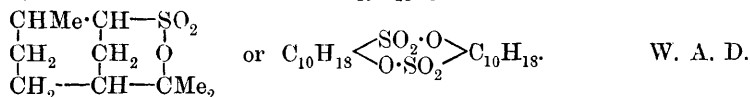
Thioborneol (camphyl hydrosulphide), $\text{C}_{10}\text{H}_{17}\cdot\text{SH}$, prepared either by reducing camphane-2-sulphonic bromide with tin and hydrochloric acid or by adding powdered sulphur to an ethereal solution of magnesium camphyl chloride, boils at 205—215° and separates from dilute alcohol as a white, crystalline mass which soon becomes caked to a glassy product; it softens gradually when heated, without melting at any definite temperature; at 50°, it is completely liquid. By air it is oxidised to *camphyl disulphide*, $(\text{C}_{10}\text{H}_{17})_2\text{S}_2$, which separates from dilute alcohol in flocculent masses of crystals and melts (when not fully purified) at 121°. The *mercuric chloride* derivative, $\text{C}_{10}\text{H}_{17}\cdot\text{S}\cdot\text{HgCl}$, of thioborneol is a white powder; the *lead* derivative, $(\text{C}_{10}\text{H}_{17}\text{S})_2\text{Pb}$, forms lustrous, yellow crystals.

Methyl camphyl sulphide (*thioborneol methyl ether*), $C_{10}H_{17}\cdot SMe$, is best prepared by warming methyl iodide with an ethereal solution of the crude product of the action of sulphur on magnesium camphyl chloride; it forms a yellow oil, which boils at $110-115^\circ$, and combines with methyl iodide, giving *dimethylcamphylsulphonium iodide*, $C_{12}H_{23}SI$; this crystallises from water, undergoing but slight decomposition in the process, in colourless plates, melts at $148-148.5^\circ$, and is converted by moist silver oxide into *dimethylcamphylsulphonium hydroxide*. The latter forms hygroscopic leaflets, melts at $140-141^\circ$, and gives a crystalline *platinichloride*, $(C_{12}H_{23}S)_2PtCl_6$, which melts at $142-143^\circ$.

Camphane-2-sulphinic acid, on oxidation with potassium permanganate, gives not the corresponding sulphonic acid, but the *sulphonic acid* of a *camphane hydrate*, which is, perhaps, either

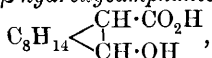


or $OH \cdot CMe \left\langle \begin{array}{c} CH(SO_3H) \cdot CH_2 \\ \text{---} CH_2 \end{array} \right\rangle CHMe_2$. The same substance is obtained on hydrolysing camphane-2-sulphonic bromide with 10 per cent. aqueous potassium hydroxide. The *potassium* salt, $C_{10}H_{19}O_4SK$, crystallises from absolute alcohol and gives, with phosphorus pentachloride, *camphane hydrate sulphonic chloride*, $C_{10}H_{19}\cdot SO_2Cl$, which forms colourless crystals and melts at about 95° . On reducing this sulphonic chloride with tin and hydrochloric acid, a *product* having the composition $C_{10}H_{18}O_3S$ is obtained, which separates from methyl or ethyl alcohol in colourless crystals and is reconverted into potassium camphane hydrate sulphonate by heating with dilute aqueous potassium hydroxide. The substance $C_{10}H_{18}O_3S$ is perhaps the *auto-ester*,



Constitution of Camphor and its Derivatives. 1X. Electrolytic Reduction of Camphorcarboxylic Acid to Borneolcarboxylic Acid and Dehydroborneolcarboxylic Acid. JULIUS BREDT [and KARL BURKHEISER] (*Annalen*, 1906, 348, 199-209).—When reduced electrolytically in potassium carbonate solution with a cathode of potassium amalgam, an *E.M.F.* of 30 volts, and a current of 7-7.5 amperes, the temperature remaining below 30° , camphorcarboxylic acid yields borneolcarboxylic acid and an *isomeride* which crystallises in needles and melts at $101-102^\circ$.

Borneolcarboxylic acid (β -hydroxycamphanecarboxylic acid),



crystallises from boiling water in silky needles, melts at $170-171^\circ$, and when quickly heated distils at 190° under 13 mm. pressure. The *calcium* salt, $(C_{11}H_{17}O_3)_2Ca$, was analysed. When repeatedly distilled slowly under 13 mm. pressure into a sealed receiver, the acid loses water and yields *dehydroborneolcarboxylic acid* (*camphenecarboxylic acid*), $C_{11}H_{16}O_2$, which crystallises in fan-like aggregates of long

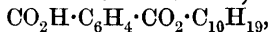
needles, melts at 112—113°, is volatile in a current of steam, and decolorises potassium permanganate, being oxidised to a crystalline acid melting at 209—210°.

Borneolcarboxylic acid is probably related to *trans*-camphylglycol (Farbwerke vorm. Meister, Lucius, & Brünig, Abstr., 1902, i, 299) as a hydroxy-acid to its glycol, dehydroborneolcarboxylic acid corresponding with dehydrocamphylcarbinol. G. Y.

Carvone. HANS RUPE (*Ber.*, 1906, 39, 2372. Compare Rupe and Dorschky, this vol., i, 595).—Carvone semicarbazone, melting at 162°, has $[\alpha]_D + 115.1^\circ$ at 20°; the semicarbazone melting at 141—142° has $[\alpha]_D + 113.3^\circ$ at 20°. W. A. D.

Action of Sodamide on Cyclic Ketones. Derivatives of Fenchone and of Camphenilone, and their Constitution. FRIEDRICH W. SEMMLER (*Ber.*, 1906, 39, 2577—2582).—*Dihydrofencholenamide* (b), $C_{10}H_{19}ON$, is obtained in quantitative yield when sodamide (1 mol.) and fenchone (1 mol.) react for four hours in boiling benzene; it melts at 94°, boils at 160° under 11 mm. pressure, and with concentrated sulphuric acid and potassium nitrite gives a brown coloration changing through red to green. A 25 per cent. ethereal solution has α_D about $+1^\circ$ in a 100 mm. tube. The substance is different from Mahla's amide (*Abstr.*, 1902, i, 106), which is subsequently called dihydrofencholenamide (a).

By hydrolysis with alcoholic potash, *dihydrofencholenic acid* (b), $C_{10}H_{18}O_2$, is obtained; it solidifies at the ordinary temperature, boils at 140—141° under 10 mm. pressure, has a sp. gr. 0.9742 at 15°, n_D 1.45862, and $\alpha_D + 3.12^\circ$ in a 100 mm. tube. The *methyl* ester, $C_{11}H_{20}O_2$, boils at 91° under 12 mm. pressure, has a sp. gr. 0.9295 at 22°, n_D 1.44260, and $\alpha_D + 3.0^\circ$ in a 100 mm. tube. The *ethyl* ester boils at 97° under 10 mm. pressure, has a sp. gr. 0.9129 at 20°, n_D 1.43958, and $\alpha_D + 3.5^\circ$ in a 100 mm. tube. Dihydrofencholenic acid (a) boils at 140.5—141° under 10 mm. pressure, has a sp. gr. 0.9742 at 20°, n_D 1.45962, and $\alpha_D + 4.10^\circ$ in a 100 mm. tube (compare Mahla, *loc. cit.*); the *methyl* ester boils at 90° under 9 mm. pressure, has a sp. gr. 0.93306 at 22°, n_D 1.44662, and $\alpha_D + 3^\circ$ in a 100 mm. tube. *Dihydrofencholenyl alcohol* (b), $C_{10}H_{20}O$, obtained in an 80 per cent. yield by reducing the ethyl ester of the acid with sodium and alcohol, boils at 100° under 11 mm. pressure, has a sp. gr. 0.8869 at 22°, n_D 1.45662, and $\alpha_D + 10^\circ$ in a 100 mm. tube; the *acetate*, $C_{10}H_{19}OAc$, boils at 112—113° under 14 mm. pressure, has a sp. gr. 0.9123 at 22°, n_D 1.44159, and $\alpha_D + 12.44^\circ$ in a 100 mm. tube; the *phthalate*,



melts at 86°, the *silver* salt at 113°.

The corresponding (a) alcohol boils at 99—100° under 10 mm. pressure, has a sp. gr. 0.9072 at 22°, and n_D 1.45762. *Dihydrofencholenaldehyde* (b), $C_{10}H_{18}O$, boils at 80—85° under 10 mm. pressure, has a sp. gr. 0.885 at 20°, and n_D 1.445; the *semicarbazone* melts at 144—145°.

When camphenilone is treated with sodamide in benzene solution, *dihydrocamphoceanamide* (*b*), $C_9H_{17}ON$, is obtained; it melts at 168° , and by hydrolysis with alcoholic potash yields the *acid* (*b*), $C_9H_{16}O_2$, which boils at $138-139^\circ$ under 12 mm. pressure, has a sp. gr. 0.9815 at 22° , and n_D 1.45662. C. S.

Synthesis of $\Delta^{8(9)}$ -Menthene and of Active $\Delta^{3,8(9)}$ -Menthadiene.

FRIEDRICH W. SEMMLER and CH. RIMPEL (*Ber.*, 1906, **39**, 2582—2587).—*isoPulegyl chloride*, $C_{10}H_{17}Cl$, is obtained quantitatively when *isopulegole* (1 mol.) dissolved in light petroleum is slowly added to phosphorus pentachloride (1 mol.) in the same solvent, rise of temperature being avoided; it boils at $85-90^\circ$ under 12 mm. pressure, has a sp. gr. 0.9600 at 20° , n_D 1.47740, $\alpha_D + 19.15^\circ$ (100 mm. tube), and by treatment with alcoholic potash yields *isopulegyl ethyl ether*, $C_{10}H_{17}OEt$, which boils at $85-88^\circ$ under 14 mm. pressure and has a sp. gr. 0.8972 at 20° .

$\Delta^{8(9)}$ -*Menthene*, $C_{10}H_{18}$, is obtained when *isopulegyl chloride* is treated with sodium and boiling alcohol. It boils at $53-55^\circ$ under 14 mm. pressure, has a sp. gr. 0.8104 at 20° , n_D 1.45662, and is optically inactive. By oxidation with dilute permanganate, it yields *p-menthane-8:9-diol*, $C_{10}H_{18}(OH)_2$, which boils at 165° under 26 mm. pressure, and is oxidised by chromic acid to *p-methylhexahydroacetophenone*, $C_9H_{16}O$, which boils at $70-73^\circ$ under 13 mm. pressure, has a sp. gr. 0.8982 at 20° , n_D 1.44561, is optically inactive, forms a *semi-carbazone*, $C_{10}H_{19}ON_3$, melting at $164-165^\circ$, and is oxidised by bromine in alkaline solution to *p-hexahydro-toluic acid*, $C_8H_{14}O_2$, which melts at 108° .

$\Delta^{3,8(9)}$ -*Menthadiene*, $C_{10}H_{16}$, is the chief product obtained when *isopulegyl chloride* dissolved in quinoline is added to quinoline at $200-210^\circ$; it boils at $62-65^\circ$ under 14 mm., or at $174-177^\circ$ under the ordinary pressure, has a sp. gr. 0.8420 at 20° , n_D 1.48422, and $\alpha_D + 15^\circ$ (100 mm. tube). The presence of a conjugated system of two double linkings is proved by the fact that the hydrocarbon absorbs only two atoms of bromine.

The physical properties of Perkin's compounds (*Trans.*, 1905, **87**, 639; 1906, **89**, 839) do not agree with the preceding data; the discrepancy is attributed to intramolecular change, which occurs in the synthesis of Perkin's $\Delta^{8(9)}$ -menthene and $\Delta^{3,8(9)}$ -menthadiene.

C. S.

Synthesis of Menthene. OTTO WALLACH (*Ber.*, 1906, **39**, 2504—2505. Compare Semmler, preceding abstract; Perkin, *Trans.*, 1906, **89**, 837).—*Ethyl 1-hydroxy-4-methylcyclohexane-1-isobutyrate*, $CHMe \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} C \cdot (OH) \cdot CMe_2 \cdot CO_2Et$, formed by condensation of 1-methylcyclohexane-4-one with ethyl α -bromoisobutyrate in presence of zinc, boils at $148-150^\circ$ under 16 mm. pressure, and on elimination of water yields *ethyl 4-methyl- Δ^1 -cyclohexene-1-isobutyrate*,

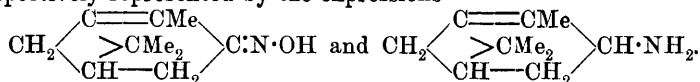


which boils at $123-126^\circ$ under 13 mm. pressure. The crystalline acid, $\text{C}_{11}\text{H}_{18}\text{O}_2$, obtained on hydrolysis of the unsaturated ester, melts at $95-96^\circ$, and when distilled slowly loses carbon dioxide and forms *i*- $\Delta^{4(8)}$ -menthene, $\text{CHMe} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{C} \cdot \text{CMe}_2$. This boils at $172-174^\circ$, has a sp. gr. 0.831 and n_D 1.4647 at 21° , and when oxidised with permanganate yields 1-methylcyclohexane-4-one and acetone. The action of amyl nitrite and hydrochloric acid, or successively of hydrochloric and nitrous acids, on *i*- $\Delta^{4(8)}$ -menthene leads to the formation of an additive compound, which is obtained as a blue oil, gradually solidifying to white crystals melting at $101-103^\circ$. Both forms of the substance are volatile in a current of steam and yield a menthylamine when reduced. When boiled with dilute sulphuric acid, *i*- $\Delta^{4(8)}$ -menthene is converted slowly into *i*- Δ^3 -menthene. G. Y.

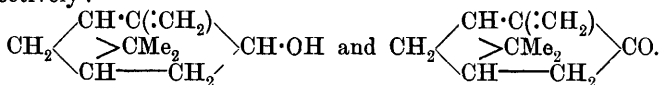
Terpenes and Ethereal Oils. LXXVIII. Pinene Series. OTTO WALLACH (*Annalen*, 1906, 346, 220—247. Compare Abstr., 1894, i, 45; 1898, i, 485; this vol., i, 370).—The nitrosopinene obtained by the action of alkalis on pinene nitrosochloride is the oxime of an unknown ketone. Attempts have now been made to ascertain which is the ketone corresponding with this oxime, and secondly to determine the chemical relations of pinocarvone, which is obtained from nitrosopinene by conversion into pinylamine and thence into a ketone.

[With FRIEDRICH JÄGER.]—Pinocarveol is prepared by treating a solution of pinylamine with acetic acid and sodium nitrite, warming, and distilling the alcohol in steam; it has still to be separated from small quantities of nitrite and unchanged pinylamine; it is a colourless oil, boiling at $100-102^\circ$ under 12 mm. pressure, and has a sp. gr. 0.980 and n_D 1.4988 at 18° . The value of the molecular refraction shows that under this treatment the ring in pinylamine is not broken. With phenylcarbimide, pinocarveol yields mainly a well-crystallised product, melting at $82-84^\circ$, together with a small amount of a compound melting at 95° . When heated with a hydrogen sulphate or with sulphuric acid or with a solution of sulphuric acid in acetic acid, cymene is obtained in small quantity from pinocarveol. On oxidation with dilute permanganate, small amounts of a glycol and an acid, $\text{C}_9\text{H}_{14}\text{O}_4$, are formed. Pinocarvone is prepared from the alcohol in the manner previously described (Abstr., 1894, i, 45), and purified by conversion into the semicarbazone, which melts at 204° . The ketone boils at 95° under 12 mm. pressure, has a sp. gr. 0.984, and n_D 1.5050 at 20° ; from the value of the molecular refraction it is concluded that pinocarvone is the enolic form of a ketone with one ethylene linking. Pinocarvoneoxime (m. p. 98°) yields on reduction with sodium and alcohol a base isomeric with but different from pinylamine; it boils at $87-88^\circ$ under 12 mm. pressure, and gives a carbamide which crystallises in needles melting at $99-100^\circ$. When oxidised with potassium permanganate, oxalic acid and a dibasic acid, $\text{C}_9\text{H}_{14}\text{O}_4$, are produced;

the latter melts at 96—97° and boils at 170—180° under 12 mm. pressure. This acid is also formed by oxidation of pinocarveol, and appears to be identical with pinic acid. On this assumption, and using Wagner's formula for pinene, nitrosopinene and pinyamine are respectively represented by the expressions



Since the reduction of pinocarvoxime yields not pinyamine but an isomeride, it follows that in the replacement of the amino-group by hydroxyl a change in the linking must have taken place. Hence the following formulæ are suggested for pinocarveol and pinocarvone respectively :



The formation of pinic acid and of cymene is then easily accounted for, but it is not obvious why the piceane ring of pinocarvone does not open with formation of carvone.

An optically active pinocarveol is contained in the less volatile fraction of the oil of *Eucalyptus globulus*, and is isolated by conversion into the hydrogen phthalate; it boils at 92° under 12 mm. pressure, has a sp. gr. 0.9745 and n_D 1.49630 at 20°, and $[\alpha]_D - 52.45^\circ$ in 12.75 per cent. ethereal solution. With phenylcarbimide it yields the same mixture of two compounds as does the artificial product. When oxidised with chromic acid in acetic acid solution, it is converted into a ketone, $\text{C}_{10}\text{H}_{14}\text{O}$, which yields with semicarbazide two *semicarbazones*, a soluble substance melting at 209—210°, and an insoluble, which crystallises in needles melting and decomposing at 320°. The oxime is crystalline and boils at 140° under 20 mm. pressure.

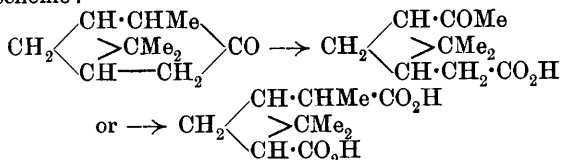
[With CURT ENGELBRECHT.]—Carvopinone is the ketone corresponding with nitrosopinene, and is obtained when the latter is digested with oxalic instead of mineral acids. It boils at 94—96° under 12 mm. pressure, and yields a characteristic *semicarbazone*, which crystallises in prisms unchanged at 300°. The ketone cannot be re-formed from the semicarbazone in a pure state. With hydroxylamine, nitrosopinene is re-formed. When reduced with sodium and alcohol, an alcohol is produced which on oxidation with chromic acid is converted into pinocamphone.

If a solution of nitrosopinene in acetic acid is boiled with oxalic acid or with 1 mol. of hydrochloric acid, it is directly converted into carvone.

Pinocamphone has been reinvestigated in order to determine whether all its reactions are in accord with the constitution at present assigned to it. With bromine, it readily yields a *dibromide*, $\text{C}_{10}\text{H}_{14}\text{OBr}_2$, which is crystalline and melts at 118—119°.

When oxidised by 1 per cent. permanganate or chromic acid in acetic acid solution, a *ketonic acid*, $\text{C}_{10}\text{H}_{16}\text{O}_3$, together with a *dibasic acid*, $\text{C}_{10}\text{H}_{16}\text{O}_4$, are produced; the ketonic acid is separated from the dibasic acid by taking advantage of its solubility in benzene, and is

shown by conversion into its semicarbazone to be identical with α -pinonic acid. The dicarboxylic acid melts at 186—187°, and is an isomeride of camphoric acid, since by acetyl chloride it is converted into an anhydride. The course of the oxidation is shown by the following scheme:



Pinyllamine can be very simply prepared² by reducing nitrosopinine with zinc and acetic acid, and, after making alkaline, distilling the base in steam. It boils at 90° under 12 mm. pressure, and has a sp. gr. 0.944 and n_D 1.5062 at 15°, and a sp. gr. 0.94 and n_D 1.5036 at 20°. The value of the molecular refraction indicates the presence of one ethylene linking.

When oxidised with a one per cent. solution of permanganate, pinyllamine does not yield pinocarveol, but carvopinone and a *monobasic acid*, $C_9H_{14}O_3$ (?), which forms crystals melting at 89° and boils at $160\text{--}170^\circ$ under 12 mm. pressure; it is not a ketonic acid, neither is it readily oxidised further by chromic acid. The absence of pinocarveol from the oxidation products of pinyllamine affords further evidence for the view that, in the change of pinyllamine into pinocarveol, a displacement of the linking takes place.

[With EDUARD ISAAC.]—Further attempts have been made in order to determine whether the nitro-compound obtained from pinene is a true pinene derivative. On reduction with zinc dust and acetic acid, a base, $C_{10}H_{17}N$, is obtained, identical with Pesci's aminoterebenthene; it boils at 95° under 12 mm. pressure, and has a sp. gr. 0.9325 and n_D 1.496 at 19° for the base prepared from *d*-pinene, whilst the base obtained from *l*-pinene has a sp. gr. 0.932 and n_D 1.4957 at 20° . Both specimens of the base are levorotatory. Methylation of the base gives the compound $C_{10}H_{15}NMe_3I$, which melts at 198° .

When the oxalate of the base is treated with nitrous acid and the alcohol thus formed oxidised with chromic acid, a compound with an odour of cuminaldehyde is produced; it yields a semicarbazone melting at 201—203°, and is oxidised by chromic acid to cumic acid (m. p. 115°). From these facts it is deduced that the base aminoterebenthene has the amino-group in the side-chain, probably having the

constitution represented by the formula $\text{CH}_2 \begin{array}{c} \text{CH} \cdot \text{C}(\text{CH}_2 \cdot \text{NH}_2) \\ > \text{CMe}_2 \\ \text{CH} \text{---} \text{CH}_2 \end{array} \text{CH}.$

Essential Oil of Rue. HENRI CARETTE (*J. Pharm. Chim.*, 1906, [vi], 24, 58—62. Compare Power and Lees, *Trans.*, 1902, 81, 1585).—The “summer oil of rue” from Algeria, prepared from *Ruta montana*, is very similar to the oil of rue prepared from *Ruta graveolens*, solidifying at 5–8° and consisting principally of methyl nonyl

ketone. Algerian "winter oil of rue," however, is obtained from *Ruta bracteosa*, solidifies at -15° to -18° , and consists almost entirely of methyl heptyl ketone; Corsican "oil of rue" is similar, being also obtained from *Ruta bracteosa*. W. A. D.

Correction. OSSIAN ASCHAN (*Ber.*, 1906, 39, 2596).—In a previous paper on the terpenes of Finnish pines and firs (this vol., i, 442), *Pinus sylvestris* and *P. abies* were incorrectly referred to as the Finland pine and the Finland fir respectively; it should have been the reverse. C. S.

Swedish Turpentine Oil. IWAN L. KONDAKOFF and IWAN SCHINDELMEISER (*Chem. Zeit.*, 1906, 30, 722—723).—From a sample of Swedish turpentine oil, the authors have isolated *p*-cymene and a small quantity of a hydrocarbon boiling at 145° , which they imagine to be either styrene or toluene. P. H.

Elemi Resins. V. ALBERT VESTERBERG (*Ber.*, 1906, 39, 2467—2472. Compare Abstr., 1887, 733; 1891, 165; 1892, 289, 290).—From Manilla elemi, Baup isolated (*Jahresb. Chem.*, 1851, 528), in addition to amyrrin, three other crystalline substances, brein, breidin, and bryoidin. The author has separated into two substances, by crystallisation from benzene, the residue in the alcoholic mother liquor from which amyrrin has been crystallised. Of these two substances, the one forms colourless, transparent tablets, melts at 216 — 217° , and appears to be Baup's brein; the other forms thick, yellow prisms and melts at 170 — 180° . Both, however, give the same acetate, $C_{30}H_{48}(OAc)_2$, which melts at 196° , evolves hydrogen bromide on treatment with bromine, and does not give an iodine number.

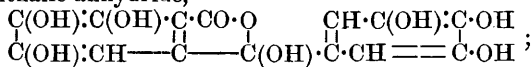
Brein, $C_{30}H_{48}(OH)_2$ (?), separates from benzene in deliquescent leaflets containing $2C_6H_6$, and from alcohol in small prisms, has $[\alpha]_D$ 65.5° at 15.5° in alcoholic solution, gives a clear yellow liquid with Liebermann's cholesterol reagent, is not affected by sodium and amyl alcohol, and is probably closely related to amyrrin, although it is not identical with oxyamyrrin. C. S.

Colouring Matter in Saffron. F. DECKER (*Chem. Zeit.*, 1906, 30, 705).—The potassium or sodium salts of crocetin are obtained by adding alcoholic potassium or sodium hydroxide to a solution of crocetin in dilute aqueous potassium or sodium hydroxide until no further precipitate is formed; on warming the respective solutions, the precipitates dissolve, and are deposited on cooling in crystalline form, the potassium salt in nodular aggregates and the sodium salt in needles. P. H.

Constitution of Tannin. J. DEKKER (*Ber.*, 1906, 39, 2497—2502).—A specimen of commercial tannin had $[\alpha]_D + 65^{\circ}$; when boiled with dilute sulphuric acid, in one hour 51.3 per cent., in two hours 73.4 per cent., and in six hours 74 per cent. of the tannin was converted

into gallic acid, the resulting solutions having $[\alpha]_D + 22^\circ$, $+ 7^\circ$, and $+ 6^\circ$ respectively.

The author considers that tannin must be represented as a derivative of phthalic anhydride,



this constitution is in accordance with the optical activity, the almost complete hydrolysis to gallic acid, the formation of diphenylmethane on distillation with zinc dust (Nierenstein, Abstr., 1905, i, 914), the formation of a hexamethyl derivative (Herzig and Tscherne, Abstr., 1905, i, 354), and the absence of a carboxyl group as shown by Boettinger (Abstr., 1884, 318) and by Walden (Abstr., 1899, i, 212).

Hexa-acetyltannin is formed, together with triacetyl gallic acid, by boiling tannin with acetic anhydride and sodium acetate; it melts at 129° and has $[\alpha]_D + 64.4^\circ$. G. Y.

Valency of the Oxygen Atom in Xanthyl Compounds. Double Salts of Xanthyl and Metallic Haloids. ROBERT FOSSE and L. LESAGE (*Compt. rend.*, 1906, 142, 1543—1545. Compare Abstr., 1905, i, 541, 917).—The author has prepared the following double salts of xanthyl (xanthonium) and metallic haloids: *xanthyl*

platinichloride, $\text{PtCl}_4 \cdot 2\text{RCl}$ [where R represents $\text{CH} \begin{smallmatrix} \swarrow \text{C}_6\text{H}_4 \\ \searrow \text{C}_6\text{H}_4 \end{smallmatrix} \text{O}$], an orange powder; *xanthyl platinibromide*, $\text{PtBr}_4 \cdot 2\text{RBr}$, an orange-yellow precipitate; *xanthyl aurichloride*, $\text{AuCl}_3 \cdot \text{RCl}$, microscopic, yellow crystals; *xanthyl auribromide*, $\text{AuBr}_3 \cdot \text{RBr}$, small, brick-red crystals; *xanthyl uranylchloride*, $\text{UO}_2\text{Cl}_2 \cdot 2\text{RCl}$, golden-yellow, prismatic crystals; *xanthyl uranyl bromide*, $\text{UO}_2\text{Br}_2 \cdot 2\text{RBr}$, yellow crystals; *xanthyl ferribromide*, $\text{FeBr}_3 \cdot \text{RBr}$, bright red, microscopic crystals; *xanthyl zincobromide*, $\text{ZnBr}_2 \cdot 2\text{RBr}$, orange-yellow crystals; *xanthyl copper bromide*, $\text{CuBr}_2 \cdot 2\text{RBr}$, small, dull violet crystals; *xanthyl cadmium bromide*, $\text{CdBr}_2 \cdot 2\text{RBr}$, small, yellow crystals; *xanthyl lead bromide*, $2\text{PbBr}_2 \cdot \text{RBr}$, small, clear brown crystals; *xanthyl mercuribromide*, $3\text{HgBr}_2 \cdot 4\text{RBr}$, golden-yellow crystals. M. A. W.

Coeroxene, its Derivatives and Isologues. HERMAN DECKER (*Annalen*, 1906, 348, 210—250. Compare Baeyer, *Ber.*, 1871, 4, 555, 658; Orndorff and Brewer, Abstr., 1900, i, 447; 1901, i, 724; Laube, this vol., i, 598).—The name coeroxene is proposed for the parent

substance, $\begin{array}{c} \text{CH—C}_6\text{H}_3\text{—} \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{C}_6\text{H}_4 \end{array} \text{O}$, of coerulein and coerulin, which become

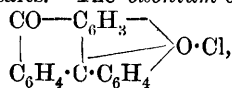
trihydroxycoeroxonone and tetrahydroxycoeroxenol respectively, and the names coeramidine and coerthiene for the isologous cyclic systems, $\begin{array}{c} \text{CH—C}_6\text{H}_3\text{—} \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{C}_6\text{H}_4 \end{array} \text{NH}$ and $\begin{array}{c} \text{CH—C}_6\text{H}_3\text{—} \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{C}_6\text{H}_4 \end{array} \text{S}$, respectively.

[With ENOS FERRARIO.]—When treated with ammonia under cooling

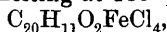
with ice, *coeroxonium sulphate*, which is prepared by the action of sulphur trioxide on fluoran dissolved in concentrated sulphuric acid below

40°, yields *coeroxonol*, $\text{CO}-\text{C}_6\text{H}_3-\text{O}$
 $\text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{C}_6\text{H}_4$, which is the carbinol base of

the coeroxonium salts. This separates from benzene, ether, chloroform, acetic acid, or acetone in colourless, strongly refracting prisms, becomes violet when heated with a solvent, darkens at 140–160°, and when quickly heated melts and decomposes at 179–180°; it dissolves in dilute mineral acids to form the blood-red oxonium salts, but is almost colourless in acetic acid solution; with dilute hydrochloric acid, an equilibrium is set up between the colourless carbinol, the acid, and the red oxonium salt. When boiled with absolute alcohol, the carbinol forms the *ethyl ether*, $\text{C}_{22}\text{H}_{16}\text{O}_3$, which separates in small, violet, shimmering crystals, melts at 145–146°, and is converted by acids into the oxonium salts. The *oxonium chloride*,



crystallises in red needles melting at 185°; the *ferrichloride*,



melts at 233°; the *mercurichloride* melts and decomposes at 228°; the *platinichloride*, $(\text{C}_{20}\text{H}_{11}\text{O}_2)_2\text{PtCl}_6$, commences to decompose at 315°; the *bromide*, $\text{C}_{20}\text{H}_{11}\text{O}_2\text{Br}$, forms red needles and melts at about 115°; the *tribromide*, $\text{C}_{20}\text{H}_{11}\text{O}_2\text{Br}_3$, forms a scarlet precipitate and loses bromine in a desiccator; the *iodide*, $\text{C}_{20}\text{H}_{11}\text{O}_2\text{I}$, melts at 216° and is very sparingly soluble; the *picrate*, *chromate*, and *nitrate* also were prepared.

3 : 13-*Dimethylcoeroxonium sulphate* is formed by the action of sulphur trioxide on dimethylfluoran in sulphuric acid solution; the *carbinol base*,

$\text{CO}-\text{C}_6\text{H}_2\text{Me}$
 $\text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{C}_6\text{H}_3\text{Me}$ $\begin{array}{l} \nearrow \\ \nearrow \\ \nearrow \end{array} \text{O}$, melts at 152°; the *ferrichloride*, $\text{C}_{22}\text{H}_{15}\text{O}_2\text{FeCl}_4$, melts at 160°.

Coeroxenol, $\text{C}(\text{OH}) \cdot \text{C}_6\text{H}_3-$
 $\text{C}_6\text{H}_4-\text{C}-\text{C}_6\text{H}_4$ $\begin{array}{l} \nearrow \\ \nearrow \\ \nearrow \end{array} \text{O}$, is prepared by the reduction of

coeroxonol in alcoholic alkaline solution, or of coeroxonium salts in acid solution by means of zinc dust, stannous chloride, or hydriodic acid, or by heating phenylxanthhenecarboxylic acid with concentrated sulphuric acid at 100°. It crystallises in yellowish-green plates, melts at 136°, dissolves in aqueous alkali hydroxides forming a red, in acetic acid forming a yellow solution with yellow fluorescence, is readily oxidised by air to coeroxonol or coeroxonium salts, and gives a red coloration and green fluorescence in concentrated sulphuric acid. The *acetyl derivative*, $\text{C}_{22}\text{H}_{14}\text{O}_3$, formed by reduction of coeroxonol in a solution containing acetic anhydride, crystallises in dark yellow leaflets, melts at 212°, is not oxidised by air, and is hydrolysed only slowly by boiling alcoholic sodium hydroxide.

Coeroxene, $\text{C}_{20}\text{H}_{12}\text{O}$, formed by boiling coeroxenol with hydriodic acid of sp. gr. 1.6 and phosphorus, crystallises in yellow leaflets, melts

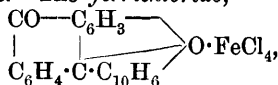
at 153°, is readily soluble in chloroform, benzene, or light petroleum, forming solutions with intense yellowish-green fluorescence, and with sulphuric acid gives a red coloration, becoming violet on heating; it is insoluble in aqueous sodium hydroxide and is not oxidised by air, but on treatment with arsenic, nitric, or chromic acid in glacial acetic acid solution forms coeroxonium salts. It is probably identical with R. Meyer and Saul's compound, formed by distilling fluoran with zinc dust (Abstr., 1893, i, 220).

[With MATEI SASSU.]—10-Phenylcoeroxene, $\begin{array}{c} \text{CPh}-\text{C}_6\text{H}_3- \\ | \quad \diagdown \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{C}_6\text{H}_4 \end{array} \text{O}$, pre-

pared by the action of magnesium phenyl bromide on coeroxonol ethyl ether, is orange-red, melts at 188°, at higher temperatures forms a fluorescent vapour, gives an orange coloration with sulphuric acid, and is stable towards feeble oxidising agents, but is oxidised, becoming scarlet, by lead dioxide or chromic or sulphuric acid in hot glacial acetic acid solution.

[With EDUARD LAUBE.]—1-Phenoxyanthraquinone, melting at 145°, is oxidised by sulphur trioxide in sulphuric acid solution at 160—180°, forming coeroxonium sulphate.

1- β -Naphthoxyanthraquinone, $\text{C}_{24}\text{H}_{14}\text{O}_3$, prepared by fusing β -naphthol with sodium α -anthraquinonesulphonate and potassium hydroxide at 170—180°, forms small, yellow crystals, melts at about 180°, gives with concentrated sulphuric acid an olive-green coloration, becoming scarlet at 100°, and when heated with 65—70 per cent. sulphuric acid at 130—150° is converted into β -benzocoeroxonium sulphate, which is only sparingly soluble. The ferrichloride,



is obtained as a black, crystalline precipitate, which melts and decomposes at 240°, and becomes blood-red when heated with concentrated sulphuric acid at 100°. The chloride and nitrate form red needles; the iodide is obtained as a dark violet, crystalline powder; the platinichloride is scarlet.

β -Benzocoeroxonol, $\begin{array}{c} \text{CO}-\text{C}_6\text{H}_3-\text{O} \\ | \quad \diagdown \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{C}_{10}\text{H}_6 \end{array}$, is readily oxidised by air;

the ethyl ether, $\text{C}_{26}\text{H}_{18}\text{O}_3$, forms almost colourless crystals and melts at 193—194°. β -Benzocoeroxonol, $\text{C}_{24}\text{H}_{14}\text{O}_2$, is yellowish-red, forms solutions with strong yellowish-red fluorescence, and is readily oxidised by air. The acetyl derivative, $\text{C}_{26}\text{H}_{16}\text{O}_3$, forms yellowish-brown crystals, melts at 206°, and is hydrolysed on prolonged boiling with alcoholic sodium hydroxide. When reduced with concentrated hydriodic acid, β -benzocoeroxonium salts yield β -benzocoeroxene, which is strongly fluorescent and is insoluble in aqueous alkali hydroxides.

α -Benzocoeroxonium sulphate is formed by oxidation of 1- α -naphthoxyanthraquinone, melting at 275—276°. The members of this series closely resemble the derivatives of β -benzocoeroxene.

[With AUGUST WÜRSCH.]—1-Phenylthioanthraquinone, $\text{C}_{14}\text{H}_7\text{O}_2 \cdot \text{SPh}$, prepared by heating thiophenol with potassium hydroxide and potassium

α -anthraquinonesulphonate at 170° , crystallises in long, yellow needles, melts at 185° , dissolves in concentrated sulphuric acid, forming a dark green solution, and yields 1-hydroxyanthraquinone when heated with dilute alkali hydroxides. When heated with 70 per cent. sulphuric acid at 160° , it is converted into the sparingly soluble, dark violet *coerthionium sulphate*. *Coerthionium ferrichloride*, $C_{20}H_{11}OSFeCl_4$, forms dark violet crystals, melts and decomposes at 227° , and is decomposed by water. The colour of these thionium salts is darker and more intense than that of the coeroxonium salts.

Coerthionol, $\begin{array}{c} \text{CO}-\text{C}_6\text{H}_3-\text{S} \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{C}_6\text{H}_4 \end{array}$, crystallises in slightly yellow prisms, melts at 220° , and dissolves in dilute acids, forming violet solutions.

Coerthienol, $\begin{array}{c} \text{C}(\text{OH}) \cdot \text{C}_6\text{H}_3- \\ | \quad | \\ \text{C}_6\text{H}_4-\text{C}-\text{C}_6\text{H}_4 \end{array} \text{S}$, formed by reduction of *coerthionol*, is yellow, dissolves in ether or alcohol, forming a solution with intense green fluorescence, and is readily oxidised to *coerthionium* salts.

[With CARL SCHENK.]—*Coeramidonine* (Damman and Gattermann, Abstr., 1902, i, 795), melting at 206° , is formed in good yield by heating *o*-acridylbenzoic acid with fuming sulphuric acid; it dissolves in concentrated sulphuric acid to a blood-red, in glacial acetic acid to a yellow, or in pyridine to a golden solution. *Coeramidonium platinichloride*, $C_{40}H_{24}O_2N_2PtCl_6$, forms glistening, red crystals and melts at 260° ; the *picrate*, $C_{26}H_{14}O_8N_4$, forms red crystals and melts at 241° . The *methosulphate* of *N*-methylcoeramidonium, formed by the action of methyl sulphate on *coeramidonine*, crystallises in small, red leaflets and dyes cotton wool mordanted with tannin a brownish-red, fast to soap. The *picrate*, $C_{27}H_{16}O_8N_4$, forms red

crystals and melts at 208° ; the *methiodide*, $\begin{array}{c} \text{CO}-\text{C}_6\text{H}_3- \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C}-\text{C}_6\text{H}_4 \end{array} \text{N}:\text{MeI}$, crystallises in brownish-red needles and melts and evolves methyl iodide at 218° ; the *nitrate* melts at $188-189^\circ$.

N-Methylcoeramidonol, $\begin{array}{c} \text{CO}-\text{C}_6\text{H}_3-\text{NMe} \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{C}_6\text{H}_4 \end{array}$, formed by treatment of the quaternary salts with sodium hydroxide, is obtained as a voluminous precipitate, crystallises from alcohol, and melts at 126° . The *ethyl* ether forms small plates and melts at 152° ; the *methyl* ether crystallises in small, deep brown leaflets with metallic lustre and melts at 155° .

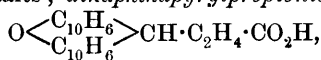
[With ENOS FERRARIO.]—*Coeramidonium* salts are formed also by the action of fuming sulphuric acid on the acridine derivatives described by Decker and Hock (Abstr., 1904, i, 450).

[With MATEI SASSU.]—*Coeramidenol*, $\begin{array}{c} \text{C}(\text{OH}) \cdot \text{C}_6\text{H}_3- \\ | \quad | \\ \text{C}_6\text{H}_4-\text{C}-\text{C}_6\text{H}_4 \end{array} \text{NH}$, is prepared by reduction of *coeramidonine* in acid, neutral, or alkaline solution; it forms a dark red solution with reddish-yellow fluorescence in ether or benzene, is soluble in aqueous alkali hydroxides, but insoluble

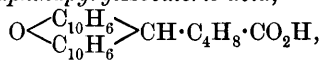
in dilute sulphuric acid, and is readily oxidised by air. The *acetyl* derivative, $C_{22}H_{15}O_2N$, forms dark red crystals, melts at 254° , has an intense yellow fluorescence in solution, and is hydrolysed by boiling aqueous alkali hydroxides. G. Y.

A Reaction of some Acid Anhydrides. New Series of Acids containing the Pyran Ring. ROBERT FOSSE (*Compt. rend.*, 1906, 143, 59—61).—Dinaphthapyranol and xanthydrol react with certain acid anhydrides with the elimination of water and the formation of the corresponding substituted acid; thus dinaphthapyranol and acetic anhydride give dinaphthapyrylacetic acid according to the equation

$$O\langle\begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix}\rangle CH\cdot OH + CH_3\cdot CO_2H = H_2O + O\langle\begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix}\rangle CH\cdot CH_2\cdot CO_2H;$$
and the following acids were thus prepared: *dinaphthapyrylacetic acid*, $O\langle\begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix}\rangle CH\cdot CH_2\cdot CO_2H$, forms beautiful, colourless crystals melting at 194° and yields crystalline *silver*, *potassium*, *sodium*, *barium*, and *calcium* salts; *dinaphthapyrylpropionic acid*,



forms colourless crystals which melt at 197° ; *dinaphthapyryl- α -isobutyric acid*, $O\langle\begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix}\rangle CH\cdot C_3H_7\cdot CO_2H$, forms colourless crystals melting at 221° ; *dinaphthapyrylisovaleric acid*,



forms colourless crystals which melt and decompose at $208\text{--}210^\circ$; *dinaphthapyrylsuccinic acid*, $O\langle\begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix}\rangle CH\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, forms beautiful, colourless crystals which melt and decompose at $225\text{--}230^\circ$; *xanthylacetic acid*, $O\langle\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}\rangle CH\cdot CH_2\cdot CO_2H$, crystallises

in beautiful, colourless needles which melt at $155\cdot5\text{--}156^\circ$, can be sublimed, and is soluble in alcohol and slightly so in boiling water; and *xanthylisovaleric acid*, $O\langle\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}\rangle CH\cdot C_4H_8\cdot CO_2H$, forms colourless crystals which melt at $147\text{--}150^\circ$. M. A. W.

Stable Derivatives of the Active Base of the Extract of Suprarenal Glands. FARBERGE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 167317).—When one mol. of the active base of the suprarenal glands is combined in aqueous solution with either boric acid (1·5 mols.) or one of its aryl derivatives (phenylboric or *m*-tolylboric acid), a stable soluble salt is produced which, on evaporation, is left as a brittle, vitreous mass having the composition $C_{18}H_{27}O_{11}N_2B_3$; when precipitated with alcohol, the salt contains one H_2O less, but both preparations have the same physiological action. The salts with phenyl- and *m*-tolyl-boric acids are pale yellow powders having similar properties. These compounds may be heated to 250°

without decomposition, and they all give a violet coloration with ferric chloride, which changes to green when this reagent is added in excess.

G. T. M.

isoConiine and the Synthesis of Coniine. ALBERT LADENBURG (*Ber.*, 1906, **39**, 2486—2491. Compare Abstr., 1893, i, 442; 1897, i, 173; Wolfenstein, Abstr., 1894, i, 627; 1895, i, 253; 1896, i, 631).—Attempts to obtain *isoconiine* as an individual substance have been unsuccessful, but it has undoubtedly a higher rotatory power than *coniine*. The fact that synthetic *coniine* has a greater rotatory power than the purest natural *d-coniine* is probably due to the presence of *isoconiine* in the former. The author has therefore repeated his former experiments and has shown that synthetic *coniine* is isomeric with *d-coniine*, being identical with it in most of its properties, but having a greater rotatory power, about 4°. It boils at 167° (corr.) and has a sp. gr. 0.8472 at 17° and 0.8445 at 20°; the anhydrous bitartrate melts at 54—55°, the hydrochloride at 221—222°, and the anhydrous platinichloride at 174°. In order to complete the synthesis of *d-coniine* it is necessary to heat the synthetic product for many hours at 290°, when pure *d-coniine* is obtained, having $[\alpha]_D^{15.67}$ at 21°.

The allylpyridine required in the synthesis is obtained by heating α -picoline, aldehyde, and water at 150°; the resulting aldol compound, $C_5NH_7 \cdot CH_2 \cdot CHMe \cdot OH$, is heated with concentrated hydrochloric acid at 185°, whereby a mixture of allylpyridine and chloropropylpyridine is obtained, which is reduced to *i-coniine* by sodium and absolute alcohol.

C. S.

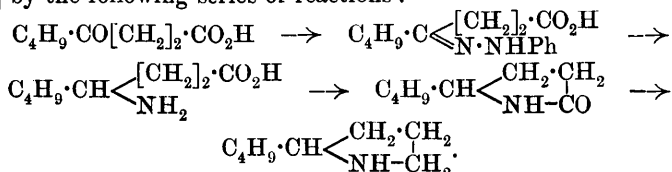
[**apoMorphine Salts.**] J. D. RIEDEL (D.R.-P. 167879. Compare Ptschorr, Abstr., 1905, i, 658).—*apoMorphine* methobromide, methochloride, and methonitrate may be produced by adding saturated aqueous solutions of potassium bromide, chloride, and nitrate respectively to the syrupy product of the action of methyl sulphate on *apomorphine* in ethereal solution; the methobromide, which at first is viscid, is rendered crystalline by dissolving in methyl alcohol and precipitating from this solution with acetone.

G. T. M.

Soluble Double Salt of Sodium Salicylate and Barium Theobromine. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 167140).—Two mols. of sodium salicylate added to a mixture of sodium theobromine (2 mols.) and barium salicylate (1 mol.) in aqueous solution give rise to a soluble *double salt* which separates on concentrating the solution under diminished pressure. G. T. M.

The Relations between Functional (Reactive) Groups in Remote Positions. Cyclic Imines. EDMOND E. BLAISE and HOUILLON (*Compt. rend.*, 1906, **142**, 1541—1543).—The existence of decamethyleneimine (compare Phookan and Krafft,

Abstr., 1892, 1180) affording evidence in favour of the view that there exists a periodicity in the closing of heterocyclic chains, the authors attempted to prepare octomethyleneimine by the action of heat on octomethylenediamine hydrochloride. The product obtained by this reaction was a 2-butylpyrrolidine, $C_4H_9 \cdot CH \begin{smallmatrix} \text{NH} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix}$, which has an odour closely resembling that of coniceine and boils at the same temperature as *i*-coniceine; the *platinichloride* melts at 123° , the *aureichloride* at 89° , and the *carbamide* at 152° . 2-Butylpyrrolidine prepared as above is identical with the synthetical compound obtained from β -butyrylpropionic acid [δ -propyl-lævulic acid or γ -keto-octoic acid] by the following series of reactions:



In view of the fact that octomethylenediamine hydrochloride on heating suffers an intramolecular migration with the formation of a pyrrolidine base, the authors suggest that Phookan and Krafft's (*loc. cit.*) decamethyleneimine is probably 2-hexylpyrrolidine.

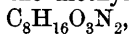
M. A. W.

Constitution of Hæmopyrrole. WILLIAM KÜSTER [with KARL HAAS] (*Annalen*, 1906, **346**, 1—27).—Since hæmatin on oxidation yields a substituted maleimide, it was to be expected that hæmopyrrole would yield an acid amide from the nature of which the constitution of hæmopyrrole could be deduced. Recent investigation of hæmamic acid (Küster) appears to show that hæmopyrrole is either methylpropylpyrrole or 3:4-diethylpyrrole, or possibly a mixture of the two.

The oxidation of hæmopyrrole yielded no definite results, although the products resembled a di-substituted maleimide and gave a barium salt similar to barium methylethylmaleate. A crystalline imide, soluble in ether and melting at 63° , was also isolated; methylpropylmaleimide melts at 56 — 57° . Hydrolysis of the imide yielded an oily anhydride, resembling in odour a disubstituted maleic anhydride; but the substance could not be purified.

Methylpropylmaleic anhydride, $C_8H_{10}O_3$, is prepared by treating ethyl propylacetoacetate in ethereal solution with an aqueous solution of potassium cyanide and hydrochloric acid; the methylpropylmalic acid which is obtained by hydrolysing the product is then heated with acetic anhydride at 240° ; the anhydride is an oil boiling at 241 — 242° (corr.) under 760 mm. pressure and has a sp. gr. 1.098 at 15° , and $K = 0.0073$. Of the corresponding acid, which could not be isolated, the *barium*, *strontium*, and *calcium* salts crystallise in leaflets with H_2O ; the *copper* salt and *silver* salts are anhydrous and amorphous.

The *ethyl* ester prepared from the silver salt is an oil decomposing at 190°. An *ammonium* salt of the methylpropylmaleamide,



is formed when dry ammonia is passed into an ethereal solution of the anhydride.

Methylisopropylmaleic anhydride, prepared similarly to the compound last described from ethyl isopropylacetoacetate, is a pale yellow oil, boiling at 240—242°. The *barium* salt of the corresponding acid, $\text{C}_8\text{H}_{10}\text{O}_4\text{Ba}, \text{H}_2\text{O}$, crystallises in leaflets, the *copper* and *silver* salts are

amorphous. Xeronic acid, $\begin{array}{c} \text{CEt}\cdot\text{CO} \\ | \\ \text{CEt}\cdot\text{CO} \end{array} \text{>O}$, was prepared by distilling citraconic acid rapidly at 200°; its boiling point was found to be 239—240°.

Methylpropylmaleimide, prepared by heating the anhydride with alcoholic ammonia at 130°, crystallises in needles melting at 56—57°. The corresponding *isopropyl compound* is prepared in a similar manner, and is a pale yellow, crystalline solid melting at 44—45°. Attempts to prepare the corresponding xeronimide did not lead to the formation of a crystalline product.

The reduction of methylpropylmaleic anhydride with zinc dust and acetic acid led to the formation of the fumaroid methylpropylsuccinic acid (m. p. 156—158°); reduction with sodium or aluminium amalgam in acid solution gave the same result. The corresponding *methylisopropylsuccinic acid* is obtained from the corresponding anhydride; it sinters at 165° and melts at 171°.

On reducing hæmin with hydriodic acid in acetic acid solution, hæmopyrrole is formed and isolated by distillation in steam. The distillate is immediately oxidised with chromic acid, and the product isolated by extraction with ether after neutralisation with sodium carbonate. Finally a crystalline substance containing nitrogen was isolated; it melted at 63—64°. The alkaline liquor, which had been extracted with ether, contained a substance melting at 93—96° which had all the properties of hæmatic acid.

K. J. P. O.

3-Benzoylpicolinic Acid. ALFRED KIRPAL (*Monatsh.*, 1906, 27, 371—377. Compare Bernthsen and Mettegang, *Abstr.*, 1887, 737; Meyer, this vol., i, 358).—3-Benzoylpicolinamide,



is formed from the acid by treatment with thionyl chloride and careful addition of the resulting acid chloride to strongly cooled, aqueous ammonia; it crystallises in quadratic plates, melts at 175°, and is hydrolysed only slowly by boiling water. 2-Amino-3-benzoylpyridine, $\text{NH}_2\cdot\text{C}_5\text{NH}_3\cdot\text{COPh}$, prepared by the action of bromine on the amide in sodium hydroxide solution, crystallises in yellow needles, melts at 145°, and when boiled with sodium nitrite in dilute sulphuric acid solution yields 2-hydroxy-3-benzoylpyridine, $\text{OH}\cdot\text{C}_5\text{NH}_3\cdot\text{COPh}$; this is formed also by heating 2-hydroxynicotinyl chloride with benzene and aluminium chloride. It crystallises in colourless needles, melts at 149°, and gives a rose coloration with aqueous ferric sulphate.

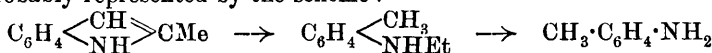
2-Hydroxynicotinyl chloride, $\text{OH}\cdot\text{C}_5\text{NH}_3\cdot\text{COCl}$, prepared by the action

of thionyl chloride on the acid, crystallises in short, yellow needles, melts and decomposes at 225° , and loses hydrogen chloride, forming the *anhydride*, on prolonged heating at 100° .

Methyl 2-hydroxynicotinate, $C_6H_4O_3NMe$, prepared by the action of methyl alcohol on the acid chloride or by boiling the acid with methyl alcohol and a few drops of concentrated sulphuric acid, crystallises from benzene in colourless needles and melts at 153° . G. Y.

Formation and Decomposition of the Indole Nucleus by the Catalytic Action of Nickel. ORESTE CARRASCO and MAURICE PADOA (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 699—703. Compare this vol., i, 530).—At temperatures up to about 200 — 250° , and in presence of hydrogen, finely-divided nickel acts as a hydrogenating agent, whilst at higher temperatures the same catalytic agent tends towards dehydrogenation, even when hydrogen itself is present.

Thus, when a mixture of hydrogen and indole vapour is passed over reduced nickel maintained at about 200° , the indole undergoes reduction and loses a carbon atom, forming *o*-toluidine. Under similar conditions, 2-methylindole also yields *o*-toluidine, the changes being probably represented by the scheme :

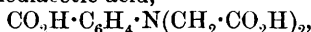


On the other hand, when the vapour of methyl-*o*-toluidine is passed over finely-divided nickel heated at 300 — 330° , it undergoes de-methylation and gives rise to indole ; no indoline is formed in this reaction.

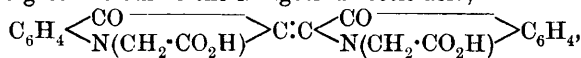
T. H. P.

Preparation of Indoxyl and its Homologues. LÉON LILIENTHAL (D.R.-P. 166447).—The aromatic glycines when condensed with the alkali hydroxides furnish only a very poor yield of indoxyl. An intimate mixture of potassium glycinate with dry potassium hydroxide and calcium hydroxide or magnesia is heated at 150 — 300° in a current of ammonia. The yield of indoxyl is in this way increased from 10 to 35 or 40 per cent., depending on the way in which the gas is introduced into the fused mass ; the more intimate the mixing the higher the yield. G. T. M.

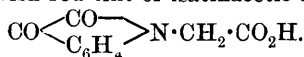
Preparation of Indoxyl. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 168292).—Anthranilodiacetic acid,



is heated for twelve hours with strong sodium hydroxide solution, the mixture then diluted considerably, and oxidised by a current of air until the green colour of the indigotindiacetic acid,



changes to the yellowish-red tint of isatinacetic acid,



The last of these compounds is converted into phenylglycine-*o*-carboxylic acid when the solution is evaporated, the product separating in

the form of its sodium salt, which can be used in preparing indoxyl and indigotin.
G. T. M.

Constitution of the Indole Group in Albumin. III. Oxidation of Tryptophan to Indole-3-aldehyde. ALEXANDER ELLINGER (*Ber.*, 1906, **39**, 2515—2522. Compare Abstr., 1904, i, 639; 1905, i, 827).—It follows from the constitution of Nencki's scatole-acetic acid (indole-3-propionic acid) that tryptophan must be scatole-3- α -aminopropionic, $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$, or scatole-

3- β -aminopropionic acid, $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{C} \cdot \text{CH}(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$.

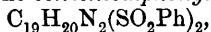
When oxidised by Hopkins and Cole's method (Abstr., 1903, i, 590), tryptophan yields *indole-3-aldehyde*, $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{C} \cdot \text{COH}$, which crystallises in colourless plates, melts at 195° , and when heated with 20 per cent. sulphuric or hydrochloric acid forms a red *dye*; this crystallises in needles, melts at about 175° , and gives a characteristic absorption spectrum resembling, but not identical with, that of the scatole dye from urine. The aldehyde interacts with hippuric acid, sodium acetate, and acetic anhydride, forming an azlactone (compare Erlenmeyer, jun., Abstr., 1902, i, 595), and when oxidised with permanganate in alkaline solution yields indole-3-carboxylic acid.

The action of chloroform and potassium hydroxide in alcoholic solution on indole leads to the formation of indole-3-aldehyde and 3-chloroquinoline (Edinger, Abstr., 1897, i, 103), which boils at 141° under 15 mm. pressure and yields an *aurichloride*, $\text{C}_9\text{NH}_6\text{Cl} \cdot \text{HAuCl}_4$, melting at 173° .
G. Y.

Action of Formaldehyde (Methanal) on Tetrahydroquinoline. R. A. WEERMAN (*Rec. trav. chim.*, 1906, **25**, 260—270).—Formaldehyde and tetrahydroquinoline readily condense at the ordinary temperature or on warming to form a yellow oil which probably contains the *aminoalcohol*, $\text{C}_9\text{NH}_{10} \cdot \text{CH}_2 \cdot \text{OH}$, for on treatment with hydrogen cyanide it yields the *nitrile*, $\text{C}_9\text{NH}_{10} \cdot \text{CH}_2 \cdot \text{CN}$, in the form of a colourless, thick oil, which boils at 193 — 195° under 7 mm. pressure, and is saponified by means of an alcoholic solution of sodium hydroxide to form *tetrahydroquinolinoacetamide*, $\text{C}_9\text{NH}_{10} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$, which crystallises from alcohol in white needles melting at 153 — 154° . Tetrahydroquinolinoacetonitrile can also be prepared by the method of Knoevenagel (Abstr., 1904, i, 989), by heating a mixture of tetrahydroquinoline, formaldehyde, and sodium hydrogen sulphite, and treating the resulting crystalline acid with potassium cyanide.

If the yellow oil obtained by the condensation of tetrahydroquinoline and formaldehyde is kept, it becomes crystalline, and the chief product is *di-1-tetrahydroquinolylmethane*, $\text{CH}_2(\text{C}_9\text{NH}_{10})_2$, which crystallises from ether or light petroleum in large, rhombic prisms melting at 61 — 62° , and is converted by the action of mineral acids into the isomeride *di-6-tetrahydroquinolylmethane*, $\text{CH}_2(\text{C}_9\text{NH}_{10})_2$; this base crystallises from ether or absolute alcohol in yellow needles,

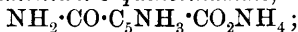
and melts at 130° , the *hydrochloride*, $C_{19}H_{22}N_2 \cdot 2HCl$, melts and decomposes at 255° , and the *benzenesulphonyl* derivative,



crystallises from alcohol or acetone in needles and melts at $185-186^\circ$. In addition to ditetrahydroquinolylmethane there is also formed a small quantity of a third *isomeride*, $C_{19}H_{22}N_2$, which is sparingly soluble in ether and forms thin, prismatic needles, which melt at 120° and yield formaldehyde when heated with dilute sulphuric acid; its constitution is at present undetermined. M. A. W.

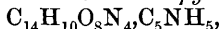
Quinolinic Esters. ALFRED KIRPAL (*Monatsh.*, 1906, 27, 363—369. Compare Abstr., 1900, i, 51; 1901, i, 227; Wegscheider, Abstr., 1898, i, 30).—The mother liquor from the preparation of 2-methyl-3-hydrogen quinolinate by the action of methyl alcohol on the anhydride, contains a very small quantity of 3-methyl-2-hydrogen quinolinate, $\begin{array}{c} CH:CH \cdot C \cdot CO_2Me \\ | \\ CH:N-C \cdot CO_2H \end{array}$; this crystallises from benzene in colourless, transparent, rhombic plates [$a:b:c = 0.5928:1:0.5869$], melts at 106° , and decomposes, forming carbon dioxide and ethyl nicotinate, at 120° . It is readily soluble in the ordinary solvents, is hydrolysed only very slowly by boiling water, and forms a *copper* salt crystallising in violet-blue prisms and closely resembling copper nicotinate. A table is given showing the reactions of picolinic and nicotinic acids and of 3-methyl-2-hydrogen and 2-methyl-3-hydrogen quinolinate with a number of metallic salts.

3-Methyl-2-hydrogen quinolinate dissolves in concentrated aqueous ammonia, forming *ammonium 3-quinolinamate*,



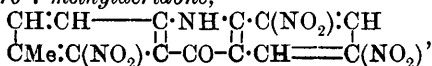
the *acid*, $C_7H_6O_3N_2$, crystallises in colourless prisms and melts at 160° , losing ammonia and forming *quinolinimide*, melting at 230° . G. Y.

1:3:6-Trinitro-7-methylacridone. SALVATORE CUTTITTA (*Gazzetta*, 1906, 36, i, 325—332).—2-*o*-Nitro-*p*-toluidino-3:5-dinitrobenzoic acid, $CO_2H \cdot C_6H_2(NO_2)_2 \cdot NH \cdot C_6H_3Me \cdot NO_2$, prepared by the action of alcoholic ammonia on a mixture of 2-chloro-3:5-dinitrobenzoic acid (1 mol.) and *o*-nitro-*p*-toluidine (1 mol.), crystallises from aqueous alcohol with $2\frac{1}{2}H_2O$ in shining, lemon-yellow plates melting at 232° and dissolves sparingly in water or acetic acid and, to a less extent, in benzene. The *ammonium* salt forms golden-yellow laminae melting at 220° and dissolves in water, benzene, alcohol, or xylene. The *sodium* salt (+ $2\frac{1}{2}H_2O$) forms small, orange-red, triclinic crystals [F. RANFALDI: $a:b:c = 1.52579:1:0.94494$; $\alpha = 76^\circ 11'$; $\beta = 81^\circ 27'$; $\gamma = 93^\circ 29'$], readily soluble in water or alcohol. The *pyridine* salt,



separates from alcohol in shining, brick-red, triclinic crystals with blue reflex [F. RANFALDI: $a:b:c = 1.35414:1:1.09430$; $\alpha = 87^\circ 16'$; $\beta = 76^\circ 36'$; $\gamma = 92^\circ 14'6''$], which melt at 200° and dissolve sparingly in benzene or water.

1:3:6-Trinitro-7-methylacridone,



prepared by the action of concentrated sulphuric acid on 2-*o*-nitro-*p*-toluidino-3:5-dinitrobenzoic acid, crystallises from acetic acid in shining, yellow plates melting at 320° and dissolves sparingly in benzene or ether and readily in xylene. Its *sodium* salt (+ 2½H₂O) crystallises from alcohol in minute, carmine needles soluble in sodium carbonate solution and is decomposed by water in the cold; on heating, it deflagrates violently.

T. H. P.

Transformations of the Quaternary Ammonium Hydroxides of Acridylpropionic Acid. CARL SCHENCK (*Ber.*, 1906, 39, 2424—2427. Compare Decker and Hock, *Abstr.*, 1904, i, 450, 620).—5-Acridyl-β-propionic acid (Volpi, *Abstr.*, 1893, i, 350) becomes brown and melts at 310°, and loses carbon dioxide when heated with zinc chloride at 250°. The *methyl* ester, C₁₇H₁₅O₂N, formed by boiling the acid with hydrogen chloride in methyl-alcoholic solution, melts at 95°, is hydrolysed slowly by boiling aqueous sodium hydroxide, and forms salts which are decomposed by water. The *iodide* forms orange needles and melts and decomposes at 205°; the *picrate*, C₂₃H₁₈O₉N₄, crystallises in glistening, yellow plates and melts at 222°. When heated with methyl sulphate at 120°, the *N*-atom of the methyl ester is methylated and the resulting *base* forms a quaternary *methosulphate*; this yields a quaternary *picrate*, C₂₄H₂₀O₉N₄, which crystallises from alcohol, melts at 210°, and is not decomposed by water, alcohol, or sodium hydrogen carbonate.

Ethyl 5-acridyl-β-propionate, C₁₈H₁₇O₂N, crystallises in long needles, melts at 83°, and is more readily hydrolysed than the methyl ester; the *picrate*, C₂₄H₂₀O₉N₄, melts at 192°.

The hydrolysis of the quaternary salts of the methylacridylpropionic esters by means of aqueous sodium hydroxide leads to the formation of the colourless, crystalline *lactone*, NMe<C₆H₄>C<C₆H₄>C<CH₂·CH₂,
O—CO

which is soluble in ether, benzene, or alcohol, and readily dissolves in water or dilute alkali hydroxides, changing into the yellow, fluorescent *betaine*, C₆H₄<C—CH₂·CH₂,
| NMe CO

; the *hydrochloride*, C₁₇H₁₆O₂NCl, formed by dissolving the lactone in hot dilute hydrochloric acid, crystallises in rosettes and melts and decomposes at 260°.

A *base*, which may be diacridylethane, is formed together with acridylpropionic acid by fusing diphenylamine with succinic acid; it forms yellow crystals, melts at about 92°, gives a yellow, fluorescent solution with concentrated sulphuric acid, and forms reddish-violet salts with mineral acids; the *picrate* melts at 113—114°. G. Y.

Derivatives of 5-Phenylacridine. III. 5-*p*-Bromophenylacridine. ALBERT E. DUNSTAN and JAMES A. STUBBS (*Ber.*, 1906, 39, 2402—2404. Compare Dunstan and Oakley, this vol., i, 383).—5-*p*-Bromophenylacridine, C₁₃H₈N·C₆H₄Br, prepared by heating *p*-bromobenzoic acid with diphenylamine and zinc chloride at 220—230°, forms greenish-yellow, prismatic crystals, melts at 234°, and dissolves in benzene, toluene, xylene, or acetic acid, less readily in

methyl or ethyl alcohol, forming fluorescent solutions. The *chromate*, $(C_{19}H_{12}NBr)_2 \cdot H_2CrO_4$, the yellow *platinichloride*, $(C_{19}H_{12}NBr)_2 \cdot H_2PtCl_6$,

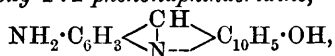
the *hydrochloride*, which crystallises in green leaflets and melts at 267° , and the *nitrate*, which forms olive-green leaflets and melts at 172° , were prepared. The *methiodide*, $C_{20}H_{15}NBrI$, prepared by the action of methyl iodide on the acridine, forms small, dark red crystals and melts and decomposes at 240° . G. Y.

Conversion of *o*-Nitro- and *op*-Dinitro-benzyl Chlorides into Acridine Derivatives. CARLO BAEZNER and J. GUEORGUIEFF (*Ber.*, 1906, **39**, 2438—2447. Compare Baezner, *Abstr.*, 1904, i, 928).—The *acetyl* derivative of 10-amino-1 : 2-phenonaphthacridine, $C_{19}H_{14}ON_2$, crystallises in yellow needles, melts at 267° , and dissolves in alcohol, forming an orange-yellow solution with violet fluorescence; the *hydrochloride* is yellow; the *platinichloride*, $(C_{17}H_{12}N_2)_2 \cdot H_2PtCl_6$, forms reddish-brown crystals; the *zincichloride*, $(C_{17}H_{12}N_2)_2 \cdot H_2ZnCl_4$, forms slender, red needles; the *chromate* is brownish-red and is insoluble. In solution the salts are yellow and have a green fluorescence.

10-Hydroxy-1 : 2-phenonaphthacridine, $OH \cdot C_6H_3 \left\langle \begin{array}{c} CH \\ | \\ N \end{array} \right\rangle C_{10}H_6$,

formed by heating the 9-amino-compound with 10 per cent. sulphuric acid in a sealed tube at 200 — 210° , crystallises from nitrobenzene in small, yellow needles, melts at about 300 — 301° , is soluble in aqueous alkali hydroxides, and dissolves in concentrated sulphuric acid or alcohol, forming a yellow solution with green fluorescence. The *hydrochloride*, $C_{17}H_{12}ONCl$, and the *sodium* salt, $C_{17}H_{10}ONNa$, are described. The *acetyl* derivative, $C_{19}H_{13}O_2N$, crystallises in white needles, melts at 160° , and has a violet fluorescence in alcoholic solution. The *benzoyl* derivative, $C_{24}H_{15}O_2N$, crystallises in small, yellow needles, melts at 186.5 — 187° , and dissolves in concentrated sulphuric acid, forming a solution with green, in alcohol forming a solution with violet, fluorescence.

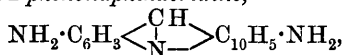
10-Amino-5-hydroxy-1 : 2-phenonaphthacridine,



is formed together with a brownish-red *substance*, which is insoluble in aqueous alkali hydroxides, by the action of stannous chloride and concentrated hydrochloric acid on 2 : 4-dinitrobenzyl chloride and 2 : 7-dihydroxynaphthalene; it crystallises from nitrobenzene in small, orange-yellow needles, melts at 180° , and dissolves in benzene or toluene, forming a yellow solution with bluish-green, in alcohol forming an orange-red solution with green fluorescence, or in mineral acids forming red solutions. The *hydrochloride*, $C_{17}H_{13}ON_2Cl$, dyes cotton-wool mordanted with tannin orange-brown. The *acetyl* derivative, $NHAc \cdot C_{17}H_9N \cdot OH$, crystallises from nitrobenzene in small, yellow needles, melts at 283 — 285° , and dissolves in aqueous alkali hydroxides. The *dibenzoyl* derivative, $C_{31}H_{20}O_2N_2$, forms small, bronze-yellow needles, melts at 212 — 215° , is insoluble in aqueous alkali hydroxides, and forms solutions in organic solvents with green to violet-blue fluorescence.

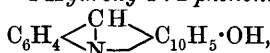
5 : 10-*Dihydroxy*-1 : 2-*phenonaphthacridine*, formed by heating 10-amino-5-hydroxy-1 : 2-phenonaphthacridine with 10 per cent. sulphuric acid in a sealed tube at 190—205°, is soluble only in aqueous alkali hydroxides ; the *dibenzoyl* derivative, $C_{31}H_{19}O_4N$, melts at 198—201°.

5 : 10-*Diamino*-1 : 2-*phenonaphthacridine*,



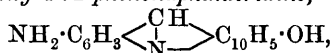
formed together with 10-amino-5-hydroxy-1 : 2-phenonaphthacridine from 2 : 4-dinitrobenzyl chloride and 7-acetyl-amino-2-naphthol, crystallises in light brown needles, melts at 180°, forms fluorescent solutions, and dyes cotton-wool mordanted with tannin brownish-red.

[With A. GARDIOL.]—4-*Hydroxy*-1 : 2-*phenonaphthacridine*,



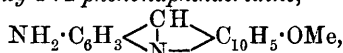
formed from *o*-nitrobenzyl chloride and 2 : 6-dihydroxynaphthalene, melts at 212°, is readily soluble in nitrobenzene, glacial acetic acid, or, forming a yellow solution, in dilute sodium hydroxide. The *hydrochloride*, $C_{17}H_{12}ONCl$, was analysed.

10-*Amino*-4-*hydroxy*-1 : 2-*phenonaphthacridine*,



formed from 2 : 4-dinitrobenzyl chloride and 2 : 6-dihydroxynaphthalene, crystallises from nitrobenzene in microscopic, yellowish-brown needles and melts at 218—220°. The *hydrochloride*, $C_{17}H_{12}ON_2 \cdot HCl$, melts at 168°. The *acetyl* derivative melts at 263°.

10-*Amino*-1-*methoxy*-1 : 2-*phenonaphthacridine*,



is formed from 2 : 4-dinitrobenzyl chloride and 2-*hydroxy*-3-*methoxynaphthalene*, which is prepared by the action of methyl sulphate on 2 : 3-dihydroxynaphthalene, crystallises in white needles, melts at 65°, and boils at about 285°. The condensation product is isolated as the *acetyl* derivative, $C_{20}H_{16}O_2N_2$, which melts at 187°, and on hydrolysis with concentrated hydrochloric acid yields the free *base*. This melts at 137°, gives an orange-brown coloration and green fluorescence with concentrated sulphuric acid, dissolves in ether or hot alcohol, forming a solution with green fluorescence, and yields a *hydrochloride* melting at 212°.

G. Y.

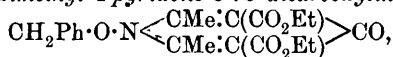
Existence of isoPyrophthalone. ALEXANDER EIBNER and M. LÖBERING (*Ber.*, 1906, **39**, 2447—2450. Compare *Abstr.*, 1903, i, 644 ; 1904, i, 921 ; von Huber, *Abstr.*, 1903, i, 576).—Pyrophthalone, obtained from phthalic anhydride and α -picoline at 200°, melts when pure at 287° ; the *sodium* derivative, $C_{14}H_8O_2NNa$, is not decomposed by water and separates from a concentrated aqueous solution in a felted mass of red needles. The *bromotribromide*, $C_{14}H_8O_2NBr_4$, forms thick, orange-yellow prisms, and is converted by alcohol, water, and ammonia at the ordinary temperature into *monobromopyrophthalone*, $C_{14}H_8O_2NBr$, which, obtained also by brominating pyrophthalone in glacial acetic acid, or the sodium derivative, crystallises

in colourless leaflets, melts at 157° , and is changed into pyrophthalone by prolonged boiling with alcohol and water or ammonia. *Anilpyrophthalone*, $C_{20}H_{14}ON_2$, prepared in benzene solution with aluminium chloride as condensing agent, separates from alcohol in felted, red needles, melts at 185° , and is decomposed by hydrochloric acid; with phenylhydrazine it yields *pyrophthalone phenylhydrazone*, $C_{20}H_{15}ON_3$, which forms reddish-brown needles and melts at 215° .

Von Huber's "isopyrophthalone," obtained from phthalyl chloride and α -picoline and melting at 280° , yields a monobromide and an anil identical with the preceding compounds, and is therefore impure pyrophthalone. From phthalyl chloride and α -picoline in benzene solution the authors have obtained pyrophthalone in the pure state, melting at 287° . C. S.

Action of Hydroxylamine on Ethyl Dimethylpyronedicarboxylate. F. CARLO PALAZZO (*Gazzetta*, 1906, 36, i, 596—611. Compare Abstr., 1904, i, 762).—The author shows that the constitution proposed by him (*loc. cit.*) for the compound $C_7H_9O_4N$, obtained by the action of hydroxylamine on ethyl dimethylpyronedicarboxylate, is erroneous, the true constitution, $O \begin{smallmatrix} \text{N} \\ \text{C}(\text{OH}) \end{smallmatrix} \begin{smallmatrix} \text{CMe} \\ \text{C} \end{smallmatrix} \text{CO}_2\text{Et}$, being that of *ethyl 5-hydroxy-3-methylisooxazole-4-carboxylate*.

The action of benzylhydroxylamine on ethyl dimethylpyronedicarboxylate differs from that of hydroxylamine, and gives rise to *ethyl 1-benzoyloxy-2:6-dimethyl-4-pyridone-3:5-dicarboxylate*,

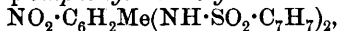


which crystallises from ethyl acetate in white, feathery needles and melts at 138° . On boiling with a dilute mineral acid, this compound is transformed into *1-hydroxy-2:6-dimethyl-4-pyridone-3:5-dicarboxylic acid*, which crystallises from alcohol in slender, white needles melting and decomposing at 245° , and gives an intense, blood-red coloration with ferric chloride. T. H. P.

Nitration of *m*-Diarylsulphondiamides. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 166600).—The *m*-diarylsulphondiamides are readily nitrated with warm dilute nitric acid, the reaction being accelerated either by efficient stirring or by the addition of an inert solvent for the diamide. The *m*-diarylsulphondiamides are prepared from the *m*-diamines by treating these bases (1 mol.) with the arylsulphonic chloride (2 mols.) in the presence of aqueous sodium carbonate.

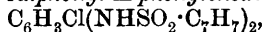
s-Ditoluene-*p*-sulphonyl-*m*-phenylenediamine, which is obtained in white crystals melting at 172° , yields *4-nitro-s-ditoluene-p-sulphonyl-m-phenylenediamine*, a brownish-yellow, crystalline substance melting at 169° .

6-Nitro-s-ditoluene-p-sulphonyl-2:4-tolylenediamine,



forms yellow crystals and melts at 210° .

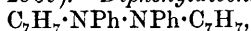
4-Chloro-s-ditoluene-p-sulphonyl-m-phenylenediamine,



separates in white prisms melting at 215° , and yields 4-chloro-6-nitro-*s*-ditoluene-*p*-sulphonyl-*m*-phenylenediamine, which crystallises in yellow prisms and melts at 196° .

s-Dibenzenesulphonyl-2 : 4-tolylenediamine crystallises in white needles melting at 191° ; its nitro-derivative is obtained in yellow prisms and melts at 185° .
G. T. M.

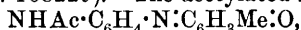
A New Method of Preparation and the Properties of Quaternary Hydrazines. HARTWIG FRANZEN and F. ZIMMERMANN (*Ber.*, 1906, 39, 2566—2569).—Diphenyldibenzylhydrazine,



obtained by boiling diphenyldibenzyltetrazone with xylene, is a faintly yellow oil which boils at $181\text{--}181.5^{\circ}$ under 19 mm. pressure, forms an unstable hydrochloride, $\text{C}_{26}\text{H}_{24}\text{N}_2\text{HCl}$, which crystallises in white needles and melts at 215.5° , and is decomposed by boiling 2*N*-sulphuric acid into aniline, benzyaniline, and benzaldehyde.

Diphenyldimethyltetrazone is decomposed in boiling xylene, forming ammonia and phenyl isocyanide.
C. S.

Acetylated Indophenols. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 168229).—The acetylated indophenol,



obtained by oxidising an alkaline solution of *p*-aminoacetanilide and *o*-cresol with sodium hypochlorite, is a reddish-brown powder, very soluble in alcohol, which crystallises from hot water in brick-red needles. A similar compound is obtained when phenol is substituted for *o*-cresol. When these substances are warmed with aqueous sodium sulphide they are simultaneously hydrolysed and reduced to leuco-derivatives.
G. T. M.

Action of Sulphuryl Chloride on Pyrazole. GIROLAMO MAZZARA and ALESSANDRO BORGO (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 704—710).—The action of sulphuryl chloride (1 mol.) on an ethereal solution of pyrazole maintained at 0° yields 4-chloropyrazole, which crystallises in the rhombic system [*C. VIOLA* : *a* : *b* : *c* = 0.8026 : 1 : 0.8284] and melts at 77° ($69\text{--}71^{\circ}$, Knorr, *Abstr.*, 1895, i, 396).

4-Chloro-1-methylpyrazole, $\text{C}_3\text{H}_2\text{N}_2\text{ClMe}$, prepared by treating a methyl-alcoholic solution of 4-chloropyrazole with methyl-alcoholic potassium hydroxide and methyl iodide, is a yellow, oily liquid, which boils at 167° under 756 mm. pressure, has a penetrating and irritating odour, and is turned red by the action of light.
T. H. P.

Researches on Pyrazolones. New Methods of Synthesis of Pyrazolones. CHARLES MOUREU and I. LAZENNEC (*Compt. rend.*, 1906, 142, 1534—1537).—Ethyl amylpropionate, $\text{C}_5\text{H}_{11}\cdot\text{C}:\text{C}\cdot\text{CO}_2\text{Et}$, and ethyl hexoacetate, $\text{C}_5\text{H}_{11}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, react with phenylhydrazine to form the same phenylamylpyrazolone melting at 96° ; similarly, the same phenylhexylpyrazolone melting at $84\text{--}85^{\circ}$ is obtained by the action of phenylhydrazine on ethyl hexylpropionate, $\text{C}_6\text{H}_{13}\cdot\text{C}:\text{C}\cdot\text{CO}_2\text{Et}$, or on methylheptoacetate, $\text{C}_6\text{H}_{13}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ (compare Rothenburg, *Abstr.*, 1893, i, 611); the phenylamylpyraz-

olone and phenylhexylpyrazolone thus prepared are isomeric with the compounds obtained by the action of phenylhydrazine on ethyl β -ethoxy- β -amylacrylate or ethyl β -ethoxy- β -hexylacrylate, which melt at 280° and 270° respectively.

Hydrazine hydrate condenses with phenylpropiolamide,
 $\text{CPh:C}\cdot\text{CO}\cdot\text{NH}_2$
 (this vol., i, 148), or with ethyl β -ethoxy- β -phenylacrylate,
 $\text{OEt}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$,

to yield a phenylpyrazolone melting at 237° , which is identical with the compound prepared similarly from ethyl phenylpropiolate or ethyl benzoylacetate (Rothenburg, *loc. cit.*).

Phenylhydrazine reacts with ethyl β -ethoxy- β -phenylacrylate to form a diphenylpyrazolone which melts at 256° and is identical with the compound prepared by Knorr by the action of heat on phenylcinnamoylhydrazine (Abstr., 1887, 665), and isomeric with the diphenylpyrazolone melting at 136° , which is formed by the action of phenylhydrazine on ethyl phenylpropiolate or ethyl benzoylacetate; it is probable that the isomeride melting at 256° is 1:5-diphenyl-3-pyrazolone, $\text{CO}\begin{smallmatrix} \text{NH}\cdot\text{NPh} \\ \text{CH}\cdot\text{CPh} \end{smallmatrix}$, formed by the elimination of $\text{C}_2\text{H}_5\cdot\text{OH}$ from the intermediate compound, $\text{OEt}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$, and that the isomeride melting at 136° is 2:5-diphenyl-3-pyrazolone, $\text{CO}\begin{smallmatrix} \text{NPh}\cdot\text{NH} \\ \text{CH}=\text{CPh} \end{smallmatrix}$, similarly formed from the intermediate compound, $\text{NHPh}\cdot\text{NH}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ (compare Buchner, Abstr., 1890, 156, and Rothenburg, *loc. cit.*).
 M. A. W.

Preparation of Cyclic Carbamide Derivatives (Pyrimidines).

EMANUEL MERCK (D.R.-P. 170555, 170657).—4-Amino-2:6-dihydroxypyrimidine is obtained by adding ethyl cyanoacetate to a mixture of acetylcarbamide and sodamide in xylene; the mixture, which is cooled during the addition of the ester, is afterwards heated at 150° for five to six hours, when the product is treated with water and the pyrimidine precipitated with acetic acid.

4-Amino-2:6-dihydroxy-3-methylpyrimidine is prepared similarly from acetylmethylcarbamide, sodamide, and ethyl cyanoacetate; the final aqueous extract contains its sodium salt, and the free pyrimidine is precipitated with acetic acid.

The foregoing pyrimidine can also be prepared from the same reagents, using, however, instead of sodamide, a solution of sodium ethoxide in absolute alcohol.
 G. T. M.

Preparation of 5:5-Dialkylbarbituric Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 163136. Compare this vol., i, 538).—Dialkylmalonodiamides and alkyl carbonates condense in presence of alkali ethoxides to form 5:5-dialkylbarbituric acids; as $\text{CEt}_2(\text{CO}\cdot\text{NH}_2)_2 + \text{CO}(\text{OEt})_2 = 2\text{EtOH} + \text{CEt}_2\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{smallmatrix}\text{CO}$. Alkali hydroxides cannot be substituted for ethoxides, as decomposition then takes place.
 C. H. D.

Preparation of 5:5-Diethylbarbituric Acid. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 167332).—Although at 100° diethylmalonamide and carbonyl chloride interact to form large quantities of diethylmalononitrile, whilst the carbamide is not produced, yet when the condensation is carried out at 150° less of the nitrile is formed, whilst a 30 to 40 per cent. yield of the carbamide derivative is obtained. The residue when crystallised from water yields pure diethylbarbituric acid melting at 191°.

G. T. M.

Preparation of Dialkylbarbituric Acids and Dialkyloxy-pyrimidine Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 168406, 168407. See preceding abstracts).—The alkyl or aryl carbonates and dialkylmalonamides condense to form substituted barbituric acids when heated in contact with sodium or sodamide. Thus diethylbarbituric acid may be obtained from ethyl carbonate and diethylmalonamide and dipropylbarbituric acid from phenyl carbonate and dipropylmalonamide.

Diethylthiobarbituric acid may be prepared by heating diethylmalonamide, carbon disulphide, and sodium ethoxide in alcoholic solution at 100°. The product is crystallised from water.

Diethylbarbituric and dipropylbarbituric acids are formed when diethylmalonamide and dipropylmalonamide respectively are heated at 100° with carbon oxysulphide and alcoholic sodium ethoxide.

G. T. M.

Pyrimidines. Synthesis of *iso*Barbituric Acid and of 5-Hydroxycytosine. TREAT B. JOHNSON and ELMER V. MCCOLLUM (*J. Biol. Chem.*, 1906, i, 437—449. Compare Abstr., 1903, i, 526).—A mixture of ethyl formate and ethyl ethylglycollate reacts with sodium suspended in ether, yielding the sodium derivative of *ethyl β-hydroxy-α-ethoxyacrylate*, $\text{NaO}\cdot\text{CH}\cdot\text{C}(\text{OEt})\cdot\text{CO}_2\text{Et}$, which condenses with an aqueous solution of *ψ*-ethylthiocarbamide hydrobromide and potassium hydroxide, yielding 6-*oxy-5-ethoxy-2-ethylthiopyrimidine*, $\text{SEt}\cdot\text{C}\begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{N}-\text{CH} \end{smallmatrix} \gg \text{C}\cdot\text{OEt}$. This crystallises from alcohol in rhombic prisms, melts at 169°, and is only sparingly soluble in hot water. It is not decomposed when boiled with hydrochloric or hydrobromic acid; with 20 per cent. hydrochloric acid at 150° it yields ethyl chloride, ethyl mercaptan, *isobarbituric acid*, and probably 2:6-dihydroxy-5-ethoxypyrimidine. A good yield of *isobarbituric acid* is obtained when the pyrimidine derivative is hydrolysed with concentrated hydrochloric acid at 150°.

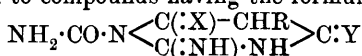
6-*Chloro-5-ethoxy-2-ethylthiopyrimidine*, $\text{SEt}\cdot\text{C}\begin{smallmatrix} \text{N}\cdot\text{CCl} \\ \text{N}\cdot\text{CH} \end{smallmatrix} \gg \text{C}\cdot\text{OEt}$, obtained by the action of phosphorus oxychloride on the corresponding oxypyrimidine, crystallises in colourless prisms, melts at 46°, and distils at 185° under 25 mm. pressure. It forms an additive compound with phosphorus oxychloride, which is decomposed by hot water. Alcoholic ammonia reacts with the chloro-derivative at 150—160°, yielding 6-*amino-5-ethoxy-2-ethylthiopyrimidine*, $\text{C}_8\text{H}_{13}\text{ON}_3\text{S}$, which

crystallises from hot water in rhombic prisms melting at 105° . The amino-compound is decomposed by 20 per cent. hydrochloric acid at 150 — 160° into ethyl mercaptan and isobarbituric acid, together with the intermediate products 5-ethoxycytosine and 2:6-dioxy-5-ethoxypyrimidine, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{OEt}$, which crystallises from water in radiating prisms, begins to turn brown at 220° , and decomposes at 260 — 280° . 5-Ethoxycytosine, $\text{CO} \begin{smallmatrix} \text{N} \cdot \text{C}(\text{NH}_2) \\ \text{NH} - \text{CH} \end{smallmatrix} \text{C} \cdot \text{OEt}$, is readily soluble in warm water, crystallises in slender prisms, and melts at 300° . Its *picrate* melts at 229 — 231° .

Concentrated hydrochloric acid at 150° transforms the aminoethoxy-ethylthiopyrimidine into ethyl chloride, ethyl mercaptan, a small amount of isobarbituric acid, and 5-hydroxycytosine, the *picrate* of which slowly decomposes above 240° .

6-Oxy-5-ethoxy-2-methylthiopyrimidine crystallises from alcohol in stout prisms and melts at 190° . 2-Amino-6-oxy-5-ethoxypyrimidine or 5-ethoxyisocytosine, $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{N} - \text{CH} \end{smallmatrix} \text{C} \cdot \text{OEt}$, obtained by the action of guanidine on ethyl sodio- β -hydroxy- α -ethoxyacrylate, is best purified by precipitation with mercuric chloride. The *sulphate*, $(\text{C}_6\text{H}_9\text{O}_2\text{N}_3)_2, \text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$, decomposes at 225 — 226° . The base crystallises from water in microscopical prisms and melts at 248° . J. J. S.

Preparation of Pyrimidine Derivatives. EMANUEL MERCK (D.R.-P. 170586).—Guanylicarbamide, which may have either of the following formulæ, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}(\text{NH}) \cdot \text{NH}_2$ or $\text{NH}_2 \cdot \text{CO} \cdot \text{N} \cdot \text{C}(\text{NH}_2)_2$, condenses with either ethyl cyanoacetate or ethyl hydrogen malonate to give a mixture of compounds of the pyrimidine series. The first formula would lead to compounds having the formulæ



and $\text{NH}_2 \cdot \text{C}(\text{NH}) \cdot \text{N} \begin{smallmatrix} \text{C}(\text{X}) \cdot \text{CHR} \\ \text{CO} - \text{NH} \end{smallmatrix} \text{C} \cdot \text{Y}$, whilst the second formula for guanylicarbamide would give rise to compounds having the following structure: $\text{NH}_2 \cdot \text{CO} \cdot \text{N} \cdot \text{C} \begin{smallmatrix} \text{NH} \cdot \text{C}(\text{X}) \\ \text{NH} - \text{C}(\text{Y}) \end{smallmatrix} \text{CHR}$, where R = hydrogen or an alkyl group, X and Y either oxygen or an imino-group.

G. T. M.

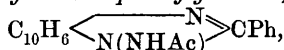
Formation of Indazyl Derivatives from *o*-Hydrazobenzoic Acid. PAUL CARRÉ (*Compt. rend.*, 1906, 143, 54—56).—The compound, $(\text{C}_{14}\text{H}_8\text{O}_2\text{N}_2)_2$, obtained by the action of water on benzaldehyde-*o*-azobenzoic acid (compare Abstr., 1905, i, 307) can be prepared more readily by treating *o*-hydrazobenzoic acid with phosphorus pentachloride (compare Freundler, this vol., i, 544). The compound yields 3-hydroxy-*o*-indazylbenzoic acid, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{OH}) \\ \text{N} \end{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, on saponification, and is regenerated from this acid by the action of dehydrating agents; it is therefore a lactone of 3-hydroxy-*o*-indazylbenzoic acid.

3-Hydroxy-o-indazylbenzoic acid crystallises from alcohol in white plates and melts at 228° with formation of the lactone; the *ethyl* ester crystallises from alcohol in white needles, melts at 132° , and decomposes at a slightly higher temperature into the lactone and ethyl alcohol.

M. A. W.

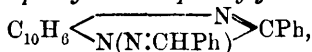
N-Aminoheterocyclic Compounds. I. 1-Amino-2-phenyl-2:3-naphthaglyoxaline. HARTWIG FRANZEN (*J. pr. Chem.*, 1906, [ii], 73, 545—569. Compare Abstr., 1905, i, 244, 830).—If 1:3-dibenzylideneamino-2-phenyldihydro-2:3-naphthaglyoxaline is boiled with glacial acetic acid and a small amount of concentrated hydrochloric acid, and the cooled liquid poured into water and distilled in a current of steam, ammonium chloride and 1-benzylideneamino-2-phenyl-2:3-naphthaglyoxaline are formed; if the distillation is continued, the latter substance is further hydrolysed to benzaldehyde and 1-amino-2-phenyl-2:3-naphthaglyoxaline, $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \text{N}(\text{NH}_2) \end{smallmatrix} \text{CPh}$. This crystallises from alcohol in small, slightly brown leaflets, melts and decomposes at 264° , dissolves readily in boiling acetone, and is a mono-acid base. Although containing the group $\text{:N}\cdot\text{NH}_2$, the properties of the base are entirely different from those of the *us.-sec.*-hydrazines. It reacts only slowly with aromatic aldehydes or phenylthiocarbimide, is not reduced by zinc dust and glacial acetic acid or oxidised when boiled with mercuric oxide and alcohol, does not react with acetone, acetophenone, aliphatic aldehydes, cyanic acid, or sodium and hydrochloric acid, and yields 2-phenyl-2:3-naphthaglyoxaline when boiled with amyl nitrite and concentrated hydrochloric acid in alcoholic solution. The *hydrochloride*, $C_{10}H_6 \begin{smallmatrix} \text{N}(\text{HCl}) \\ \text{N}(\text{NH}_2) \end{smallmatrix} \text{CPh}$, crystallises in slightly yellow needles, melts at 245° , and is decomposed by water; the *sulphate*, $(C_{17}H_{13}N_3)_2 \cdot H_2SO_4$, forms matted, yellow needles and melts at 240° ; the *nitrate*, $C_{17}H_{14}O_3N_4$, crystallises in yellow needles and melts and decomposes at 176° ; the *picrate*, $C_{17}H_{13}N_3 \cdot C_6H_3O_7N_3$, forms small, yellow needles and melts and decomposes at 205 — 206° ; the *platinichloride*, $(C_{17}H_{13}N_3)_2 \cdot H_2PtCl_6$, is obtained as a yellow precipitate.

1-Acetyl-amino-2-phenyl-2:3-naphthaglyoxaline,

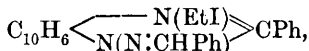


formed by boiling the base with acetic anhydride, crystallises in stout, colourless prisms and melts at 192° . *1-Phenylthiocarbamido-2-phenyl-2:3-naphthaglyoxaline*, $C_{11}H_6N_2Ph \cdot NH \cdot CS \cdot NHPh$, formed by prolonged boiling of the amino-base with phenylthiocarbimide in alcoholic solution, crystallises in slender, yellow needles and is only sparingly soluble in boiling alcohol. The *ethiodide*, $C_{10}H_6 \begin{smallmatrix} \text{N}(\text{EtI}) \\ \text{N}(\text{NH}_2) \end{smallmatrix} \text{CPh}$, prepared by boiling the base with ethyl iodide in alcoholic solution in a reflux apparatus, crystallises in rosettes of slender, yellow needles, melts and blackens at 195 — 196° , and when heated with dilute hydrochloric acid is decomposed, forming 1-amino-2-phenyl-2:3-naphthaglyoxaline hydrochloride.

1-Benzylideneamino-2-phenyl-2 : 3-naphthaglyoxaline,

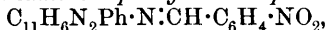


formed in the first stage of the hydrolysis of 1 : 3-dibenzylideneamino-2-phenyl-2 : 3-naphthaglyoxaline or by prolonged boiling of the 1-amino-base with benzaldehyde in alcoholic solution, crystallises in slender, yellow or yellowish-brown needles and melts at 169° ; the *hydrochloride*, $\text{C}_{24}\text{H}_{18}\text{N}_3\text{Cl}$, forms light yellow, slender needles and sinters at 210° , but does not melt at 285° ; the *sulphate*, $\text{C}_{48}\text{H}_{36}\text{O}_4\text{N}_6\text{S}$, forms slender, yellow needles and sinters at 235° , but does not melt at 285° ; the *picrate*, $\text{C}_{30}\text{H}_{20}\text{O}_7\text{N}_6$, forms slender, yellow needles and melts and decomposes at $248\text{--}249^\circ$. The *ethiodide*,



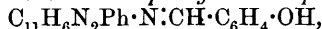
crystallises in slender, yellow needles and melts and decomposes at 218° .

1-o-Nitrobenzylideneamino-2-phenyl-2 : 3-naphthaglyoxaline,



crystallises in golden-brown needles and melts at $217\text{--}218^\circ$.

1-o-Hydroxybenzylideneamino-2-phenyl-2 : 3-naphthaglyoxaline,

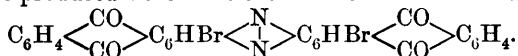


crystallises in slightly yellow needles and melts and blackens at 284° .

2-Phenyl-2 : 3-naphthaglyoxaline, $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \\ \text{NH} \end{array} \text{CPh}$, is prepared

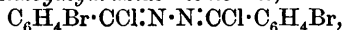
together with benzylamine and dibenzylamine by reducing the 1-benzylideneamino-compound with zinc dust and glacial acetic acid; it crystallises in small needles or leaflets and melts at $210\text{--}211^\circ$, or, after resolidification, at 192° . The *hydrochloride*, $\text{C}_{17}\text{H}_{13}\text{N}_2\text{Cl}$, forms a yellow, crystalline mass and commences to sinter at 170° , but does not melt at 285° ; the *sulphate*, $(\text{C}_{17}\text{H}_{12}\text{N}_2)_2\cdot\text{H}_2\text{SO}_4$, is obtained as a yellow, flocculent precipitate. G. Y.

Conversion of Anthracene Derivatives into Azines and Dihydroazines. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co (D.R.-P. 167255).—When 1 : 3-dibromo-2-aminoanthraquinone is heated at 150° with nitrobenzene, copper chloride, and fused sodium acetate, a compound is produced which has the constitution of an *azine*,



At 180° an appreciable amount of the dihydroazine is also formed. The azine is obtained in the form of greenish-yellow, very sparingly soluble crystals which dissolve in fuming sulphuric acid and yield a colouring matter on boiling with aniline or quinoline (compare Abstr., 1905, i, 797). G. T. M.

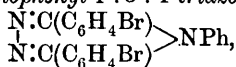
Conversion of Hydrazine Derivatives into Heterocyclic Compounds. XXI. Diacylhydrazide Dichlorides of Substituted Benzoic Acids and their Reaction Products. ROBERT STOLLÉ and ANTON WEINDEL (*J. pr. Chem.*, 1906, [ii], 74, 1—12. Compare Stollé, this vol., i, 453; Stollé and Thoma, *ibid.*, 461).—*Di-p-bromobenzoylhydrazide dichloride*,



formed together with 2:5-di-*p*-bromophenyl-1:3:4-oxadiazole by heating di-*p*-bromobenzoylhydrazide with phosphorus pentachloride at 120°, separates from ether in stout, transparent crystals, from alcohol in transparent, slightly yellow leaflets, melts at 145°, dissolves in concentrated sulphuric acid, forming a golden-yellow solution, and yields 2:5-di-*p*-bromophenyl-1:3:4-oxadiazole when heated with alcoholic silver nitrate, or more slowly when boiled with water.

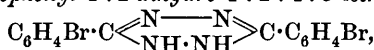
2:5-Di-*p*-bromophenyl-1:3:4-triazole, $\begin{matrix} \text{N}:\text{C}(\text{C}_6\text{H}_4\text{Br}) \\ \text{N}:\text{C}(\text{C}_6\text{H}_4\text{Br}) \end{matrix} \rangle \text{NH}$, formed by heating the dichloride with alcoholic ammonia in a sealed tube at 150°, crystallises in long needles, melts at 284°, dissolves in aqueous sodium hydroxide, and is reprecipitated by carbon dioxide, and forms a stable white *precipitate* with silver nitrate in alcoholic solution.

1-Phenyl-2:5-di-*p*-bromophenyl-1:3:4-triazole,

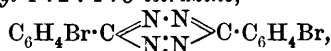


prepared by the action of aniline on the dichloride at 170°, crystallises in matted, slender needles and melts at 261°.

3:6-Di-*p*-bromophenyl-1:2-dihydro-1:2:4:5-tetrazine,



prepared by boiling the dichloride with hydrazine hydrate in ethereal solution, separates from benzene in yellow crystals, melts and decomposes at 235°, forming an intensely red liquid, and is oxidised by silver nitrate in alcoholic solution, metallic silver being precipitated, or more slowly on exposure of the alcoholic solution to air, forming 3:6-di-*p*-bromophenyl-1:2:4:5-tetrazine,

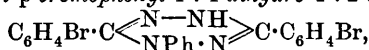


which crystallises from benzene in bluish-red leaflets and does not melt at 280°, but decomposes when more highly heated, yielding a colourless sublimate smelling of benzonitrile.

3:6-Di-*p*-bromophenyl-1:4-dihydro-1:2:4:5-tetrazine hydrochloride, $\text{C}_6\text{H}_4\text{Br}\cdot\text{C} \begin{matrix} \text{N}\cdot\text{NH} \\ \text{NH}\cdot\text{N} \end{matrix} \rangle \text{C}\cdot\text{C}_6\text{H}_4\text{Br}, \text{HCl}$, formed by the action of hydrogen chloride on the 1:2-dihydrotetrazine in alcoholic solution, crystallises in small prisms. The base, $\text{C}_{14}\text{H}_{10}\text{N}_4\text{Br}_2$, crystallises from alcohol in glistening, white needles, does not melt at 300°, and forms a stable, white *precipitate* with silver nitrate in alcoholic solution.

1:2-Dibenzoyl-3:6-di-*p*-bromophenyl-1:2-dihydro-1:2:4:5-tetrazine, $\text{C}_6\text{H}_4\text{Br}\cdot\text{C} \begin{matrix} \text{N} \text{---} \text{N} \\ \text{NBz}\cdot\text{NBz} \end{matrix} \rangle \text{C}\cdot\text{C}_6\text{H}_4\text{Br}$, prepared by the action of benzoyl chloride on the 1:2-dihydrotetrazine in pyridine solution, separates from alcohol as a yellow, crystalline powder and melts at 248°.

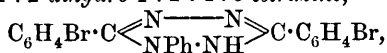
1-Phenyl-3:6-di-*p*-bromophenyl-1:4-dihydro-1:2:4:5-tetrazine,



prepared by heating di-*p*-bromobenzoylhydrazide dichloride with phenylhydrazine in alcoholic solution on the water-bath, forms small,

glistening, white, granular crystals and melts and decomposes at 260°.

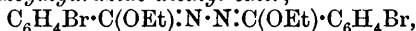
The action of phenylhydrazine on di-*p*-bromobenzoylhydrazide dichloride in pyridine solution leads to the formation of 1-phenyl-3:6-di-*p*-bromophenyl-1:2-dihydro-1:2:4:5-tetrazine,



which crystallises from alcohol in yellow needles, melts and decomposes at 167°, and forms a brown *precipitate* with silver nitrate in alcoholic solution.

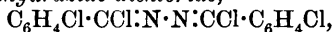
The action of *m*-nitrobenzylidenehydrazide and pyridine on di-*p*-bromobenzoylhydrazide dichloride in boiling benzene solution leads to the formation of 3:6-di-*p*-bromophenyl-1:2:4:5-tetrazine and 2:5-di-*p*-bromophenyl-1:3:4-oxadiazole.

Di-p-bromobenzoylhydrazide diethyl ether,



formed by boiling the dichloride with sodium ethoxide in alcoholic solution in a reflux apparatus, crystallises in matted, slender needles, melts at 111°, and is hydrolysed by hydrochloric acid at 150°, forming hydrazine, *p*-bromobenzoic acid, and ethyl chloride. When heated with alcoholic ammonia in a sealed tube at 200°, it forms 2:5-di-*p*-bromophenyl-1:3:4-triazole.

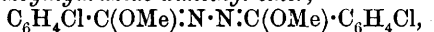
Di-p-chlorobenzoylhydrazide dichloride,



forms large, glistening crystals, melts at 125°, dissolves in ether or hot alcohol, forming green solutions, and yields silver chloride only slowly when boiled with alcoholic silver nitrate.

3:6-Di-*p*-chlorophenyl-1:2-dihydro-1:2:4:5-tetrazine, $\text{C}_{14}\text{H}_{10}\text{N}_4\text{Cl}_2$, forms yellow crystals, melts, becoming red, at 215°, and is oxidised to the *tetrazine*, which crystallises in bluish-red leaflets, by alcoholic silver nitrate at the ordinary temperature, by amyl nitrite in hot benzene solution, or more slowly on exposure of the alcoholic solution to air.

Di-p-chlorobenzoylhydrazide dimethyl ether,



melts at 162°.

2:5-Di-*o*-nitrophenyl-1:3:4-oxadiazole, $\begin{array}{c} \text{N}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NO}_2) \\ \diagup \quad \diagdown \\ \text{N}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NO}_2) \end{array} > \text{O}$, crys-

tallises in white needles and melts at 195°.

1-Phenyl-2:5-di-*m*-nitrophenyl-1:3:4-triazole, $\text{C}_{20}\text{H}_{13}\text{O}_4\text{N}_5$, crystallises in matted, white needles and melts at 215°.

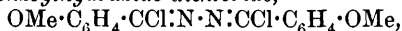
The action of phosphorus pentachloride on benzoylhydrazide leads to the formation of 2:5-diphenyl-1:3:4-triazole and a compound, $\text{NHBz}\cdot\text{NH}\cdot\text{P}(\text{N}\cdot\text{NHBz})_2$, which crystallises from alcohol and melts at about 220°.

G. Y.

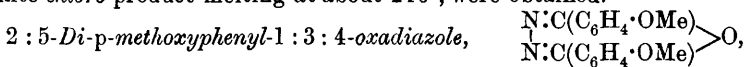
Conversion of Hydrazine Derivatives into Heterocyclic Compounds. XXII. Diacylhydrazide Dichlorides of Substituted Benzoic Acids and of α -Naphthoic Acid. ROBERT STOLLÉ and ADOLF BAMBACH (*J. pr. Chem.*, 1906, [ii], 74, 13—24. Compare Stollé, this vol., i, 453; Stollé and Thoma, *ibid.*, 461).—*Di-p-methoxybenzoylhydrazide*, $\text{C}_{16}\text{H}_{16}\text{O}_4\text{N}_2$, which forms colourless

crystals and melts at 224° , is prepared together with *p*-methoxybenzoylhydrazide by the action of anisyl chloride on hydrazine sulphate in dilute potassium hydroxide solution. The latter substance is isolated as the *benzylidene* derivative, $C_{15}H_{14}O_2N_2$, which crystallises from alcohol in white needles and melts at 198° .

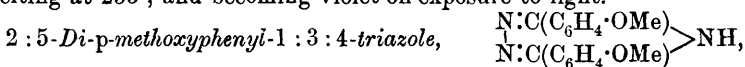
Di-p-methoxybenzoylhydrazide dichloride,



formed together with the corresponding oxadiazole, crystallises from ether or alcohol in needles or leaflets, melts at $130-150^{\circ}$, gives a golden-yellow coloration with concentrated sulphuric acid, and yields silver chloride when heated with alcoholic silver nitrate. In one preparation a compound containing chlorine and nitrogen, crystallising in green, glistening needles and melting at about 185° , and in another a white *chloro*-product melting at about 210° , were obtained.

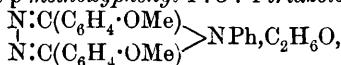


formed by heating di-*p*-methoxybenzoylhydrazide with thionyl chloride in a reflux apparatus or alone at 260° , crystallises from alcohol in glistening, white needles, melts at 164° , and forms a white, flocculent *precipitate*, $C_{16}H_{14}O_3N_2 \cdot AgNO_3$, with silver nitrate in alcoholic solution, melting at 233° , and becoming violet on exposure to light.



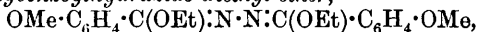
forms white leaflets or rhombic crystals, melts when slowly heated at $180-182^{\circ}$, or at 150° if suddenly heated, dissolves in hot sodium carbonate solution, and yields a white *precipitate* with silver nitrate.

1-Phenyl-2 : 5-di-p-methoxyphenyl-1 : 3 : 4-triazole,



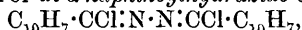
crystallises in white, silky fibres, loses C_2H_6O at 100° , melts at 250° , is slightly soluble in acids, but insoluble in aqueous alkali hydroxides, and forms a flocculent *precipitate* with silver nitrate in alcoholic solution.

Di-p-methoxybenzoylhydrazide diethyl ether,

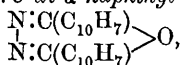


crystallises from alcohol in white needles, melts at $116-117^{\circ}$, and is hydrolysed by boiling hydrochloric acid and alcohol.

The action of phosphorus pentachloride on di- α -naphthoylhydrazide leads to the formation of *di- α -naphthoylhydrazide dichloride*,



which forms stout crystals, melts at $104-105^{\circ}$, gives an orange coloration with concentrated sulphuric acid, and is converted by silver nitrate in alcoholic solution into *2 : 5-di- α -naphthyl-1 : 3 : 4-oxadiazole*,



which forms a crystalline powder, melts at 175° , and shows a violet fluorescence in alcoholic or ethereal solution (compare Ekstrand, Abstr., 1887, 373, 840).

Di-p-nitrobenzoylhydrazide dichloride, $C_{14}H_8O_4N_4Cl_2$, crystallises from

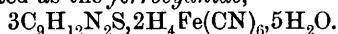
xylene or acetone in lemon-yellow needles, melts at 187° , and reacts with silver nitrate only slowly in boiling alcoholic solution.

2:5-Di-*p*-nitrophenyl-1:3:4-oxadiazole, $C_{14}H_8O_5N_4$, crystallises in glistening, yellowish-brown or rose leaflets, melts at 302° , and is only sparingly soluble in hot organic solvents.

When heated with alcoholic ammonia at 200° , the dichloride yields 2:5-di-*p*-nitrophenyl-1:3:4-triazole (Pinner, Abstr., 1898, i, 94).

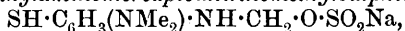
1-Phenyl-2:5-di-*p*-nitrophenyl-1:3:4-triazole, $C_{20}H_{13}O_4N_5$, separates from acetone in matted, white needles or from alcohol in small, stout crystals, melts at 270° , and forms a gelatinous additive compound with silver nitrate. G. Y.

Action of Formaldehyde on *as*-Dimethyl-*p*-phenylenediaminethiosulphonic Acid and a New Method of preparing Benzothiazoles. OTTO SCHMIDT (*Ber.*, 1906, 39, 2406—2413. Compare Rügheimer, this vol., i, 418).—*Anhydroformaldehyde dimethyl-*p*-phenylenediamine mercaptan* [5-dimethylamino-2-methyleneamino-phenyl mercaptan], $SH \cdot C_6H_3(NMe_2) \cdot N \cdot CH_2$, is formed by the action of formaldehyde and hydrochloric acid on *as*-dimethyl-*p*-phenylenediaminethiosulphonic acid dissolved in aqueous ammonia; it polymerises rapidly and is isolated as the *ferrocyanide*,



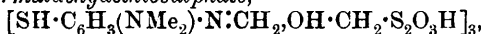
The action of sodium nitrite and hydrochloric acid on the freshly-prepared cooled solution of the mercaptan leads to the formation of 5-dimethylaminobenzothiazole, $NMe_2 \cdot C_6H_3 < \underset{S}{N} > CH$, together with a small amount of a substance, which crystallises in matted, red needles and melts at 128° . The benzothiazole is formed also by boiling *as*-dimethyl-*p*-phenylenediaminethiosulphonic acid with formic acid; it crystallises in colourless leaflets, melts at 73 — 74° , is a feeble base, and gives a greenish-blue coloration, which becomes sky-blue on addition of water, with ferric chloride.

Sodium p-dimethylaminomercaptoanilinomethylsulphite,



is formed by heating the anhydro-compound with sodium hydrogen sulphite solution at 60° ; it crystallises from concentrated sodium hydroxide solution, and when treated with sodium nitrite in dilute acetic acid solution yields 5-dimethylamino-1:2-dihydrobenzothiazyl hydrogen sulphite, $NMe_2 \cdot C_6H_3 < \underset{S}{NH} > CH \cdot O \cdot SO_2H$. This forms small, lemon-yellow leaflets or needles, does not melt at 300° , dissolves in strong acids or bases, forming coloured salts, and yields 5-dimethylaminobenzothiazole when heated or when boiled with aqueous alkali hydroxides. G. Y.

Compounds of Thiosulphuric Acid with Aldehydes. OTTO SCHMIDT (*Ber.*, 1906, 39, 2413—2419. Compare preceding abstract; Vanino, Abstr., 1902, i, 744).—5-Dimethylamino-2-methyleneamino-phenylthiol formaldehydethiosulphate,



is formed by the action of sodium thiosulphate, formaldehyde, and hydrochloric acid on dimethyl-*p*-phenylenediaminethiosulphonic acid in ammoniacal solution; it crystallises in glistening, white, rhombic leaflets, melts and decomposes at about 122°, dissolves and partially decomposes when boiled with water, and is insoluble in organic solvents. When boiled with aqueous sodium hydroxide it forms sodium thiosulphate, formaldehyde, and the trimeride of the anhydro-mercaptan. In presence of an excess of formaldehyde, sodium thiosulphate is decomposed by hydrochloric acid, forming sulphuric acid, trithioformaldehyde being formed at the same time. If the formaldehyde is not in excess, sulphur and sulphur dioxide are formed. The decomposition of the formaldehydethiosulphate by hydrochloric acid takes place in the same manner.

The formaldehydethiosulphate is converted into 5-dimethylamino-benzothiazole in the same manner as is the free anhydro-compound (preceding abstract). G. Y.

Action of Carbonyl Chloride on 4-Acetylamino-*m*-phenylenediamine. LEOPOLD CASSELLA & Co. (D.R.-P. 166680).—When carbonyl chloride is passed into a solution of 4-acetylamino-*m*-phenylenediamine in aqueous sodium carbonate, an insoluble carbamide is precipitated. This *diacetyltetra-aminodiphenylcarbamide* is insoluble in all the ordinary solvents and melts above 300°. When fused with sulphur at 240°, it yields a colouring matter containing sulphur, and soluble in alkali sulphides. G. T. M.

Colourless Soluble Salts of Rosaniline. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 163104).—Both triaminoditolylphenylcarbinol and triaminotritolylcarbinol dissolve in concentrated hydrochloric acid on a boiling water-bath, and crystals of a colourless salt separate on cooling. The product is washed with hydrochloric acid and dried in a vacuum, or, if necessary, washed with alcohol and ether. These salts dissolve very readily in cold water to form colourless solutions, which become red when heated, owing to dissociation. C. H. D.

Quinazolines. XV. A 3-Aminoquinazoline and the Corresponding 3:3'-Diquinazolyl from 6-Nitroacetylanthranil and Hydrazine Hydrate. MARSTON T. BOGERT and HARVEY A. SEIL (*J. Amer. Chem. Soc.*, 1906, **28**, 884—893. Compare Abstr., 1905, i, 945).—When 6-nitroacetylanthranil (1 mol.) is added to hydrazine hydrate (1 mol.) in 33 per cent. aqueous solution, 5-nitro-3-amino-4-keto-2-methyldihydroquinazoline,
$$\begin{array}{c} \text{CH} \cdot \text{CH} = \text{C} \cdot \text{N} = \text{C} \text{Me} \\ | \qquad \qquad | \\ \text{CH} \cdot \text{C}(\text{NO}_2) : \text{C} \cdot \text{CO} \cdot \text{N} \cdot \text{NH}_2 \end{array}$$
, is obtained; this crystallises in long, colourless prisms, melts at 152—153° (corr.), and is fairly soluble in water, alcohol, or acetone, slightly so in chloroform or benzene, and nearly insoluble in ether; the *hydrochloride* melts at 253—254° (corr.); the *platinichloride* forms yellow crystals.

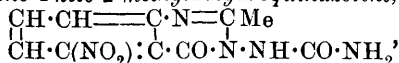
The *diacetyl* derivative,
$$\begin{array}{c} \text{CH} \cdot \text{CH} = \text{C} \cdot \text{N} = \text{C} \text{Me} \\ | \qquad \qquad | \\ \text{CH} \cdot \text{C}(\text{NO}_2) : \text{C} \cdot \text{CO} \cdot \text{N} \cdot \text{N} \cdot \text{Ac}_2 \end{array}$$
, crystallises from

warm alcohol in long, white, slender needles, melts at 233° (corr.), and yields a bromo-derivative, $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Br} \begin{smallmatrix} \text{N}=\text{CMe} \\ \text{CO} \cdot \text{N} \cdot \text{N} \cdot \text{Ac}_2 \end{smallmatrix}$, which separates from dilute alcohol in small, yellow crystals, softens at 105° , and melts at 110° (corr.).

The aminoquinazoline yields an isonitrile-like odour with chloroform and potassium hydroxide, and undergoes condensation with benzaldehyde. It dissolves in warm aqueous potassium hydroxide to a purple-red solution, which, on neutralisation with acetic acid, deposits brown crystals of a nitrogenous substance, melting at $259\text{--}260^{\circ}$ (uncorr.).

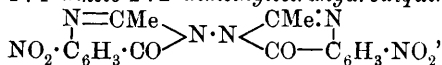
By the action of phenylhydrazine on the aminoquinazoline, 5-nitro-3-phenylhydrazino-4-keto-2-methyldihydroquinazoline phenylhydrazone, $\begin{smallmatrix} \text{CH} \cdot \text{CH} = \text{C} \cdot \text{N} = \text{CMe} \\ | \\ \text{CH} \cdot \text{C}(\text{NO}_2) \cdot \text{C} \cdot \text{C}(\text{N} \cdot \text{NHPh}) \cdot \text{N} \cdot \text{NH} \cdot \text{NHPh} \end{smallmatrix}$, is produced, which crystallises in large, white, lustrous plates and melts at $124\text{--}125^{\circ}$ (corr.).

The aminoquinazoline does not react with potassium cyanate. 5-Nitro-3-carbamino-4-keto-2-methyldihydroquinazoline,



prepared by the condensation of 6-nitroacetylanthranil with semicarbazide, melts at $263\text{--}264^{\circ}$ (uncorr.). The corresponding 7-nitro-compound, obtained from 4-nitroacetylanthranil and semicarbazide, forms masses of white, silky needles and melts at 266° (corr.); its aqueous solution gives a flocculent precipitate on the addition of bromine water; its diacetyl derivative melts at $229\text{--}230^{\circ}$ (corr.).

5:5'-Dinitro-4:4'-diketo-2:2'-dimethyltetrahydrodiquinazolyl,



obtained by adding hydrazine hydrate (1 mol.) to finely-powdered 6-nitroacetylanthranil (2 mols.) so that the latter is always in excess, separates from a mixture of alcohol and acetone in small, granular crystals, melts at 306° , is not affected by acids or alkalis, and does not yield a bromo-derivative. The diquinazolyl can also be obtained, but only in very small yield, by condensing the aminoquinazoline with another molecule of 6-nitroacetylanthranil. The substance unites with 1 mol. of acetic anhydride to form an additive compound which crystallises in cubes, softens at 223° , and melts at 228° (corr.).

E. G.

Aminohydroxy-derivatives of the Phenyl-naphthiminazoles.

AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 167139).—When a nitrobenzaldehyde reacts with one of the naphthylene-*o*-diaminedisulphonic acids in the presence of acids, a nitrobenzylidene derivative is produced, which, when reduced, yields an aminophenyl-naphthiminazoledisulphonic acid having the following formula: $\text{C}_{10}\text{H}_4(\text{SO}_3\text{H})_2 \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$. On fusion with alkali hydroxides,

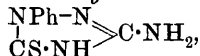
the acid loses one of its sulpho-groups, and an aminohydroxy-derivative is produced.

3'-Aminophenyl-1:2-naphthiminazole-5:7-disulphonic acid, obtained by condensing *m*-nitrobenzaldehyde and naphthylene-1:2-diamine-5:7-disulphonic acid in sodium hydrogen sulphite solution and reducing the intermediate nitro-compound with iron filings and dilute hydrochloric acid, is a yellow powder moderately soluble in water and dissolving readily in aqueous alkalis; when fused with alkali hydroxides, it yields 3'-aminophenyl-5-hydroxy-1:2-naphthiminazole-7-sulphonic acid, an almost colourless powder, which is sparingly soluble in water, but readily dissolved by aqueous alkalis.

Similar compounds are obtained from naphthylene-2:3-diamine-5:7-disulphonic acid, and the *m*-nitrobenzaldehyde may be replaced by other aldehydes, such as *p*-nitrobenzaldehyde and 3-nitro-4-dimethylaminobenzaldehyde-6-sulphonic acid. G. T. M.

Action of Phenylhydrazine on Unsaturated Disulphides. Synthesis of Triazoles. EMIL FROMM and KURT SCHNEIDER (*Annalen*, 1906, 348, 174—198).—The action of phenylhydrazine on perthiocyanic acid leads to the formation of phenyldithiourazole (3:5-dithiol-1-phenyl-1:2:4-triazole), 3-amino-5-thio-1-phenyl-4:5-dihydro-(or 5-amino-1-phenyl-3-thio-2:3-dihydro-)-1:2:4-triazole, and anilthiouret.

3-Amino-5-thio-1-phenyl-4:5-dihydro-1:2:4-triazole,



crystallises from alcohol in slender, yellow needles, melts at 134.5°, is soluble in mineral acids or dilute alkali hydroxides or ammonia, and reacts with sodium hydroxide and benzyl chloride in alcohol, forming 3-amino-5-thiobenzyl-1-phenyl-1:2:4-triazole, $\text{NH}_2\cdot\text{C}_2\text{N}_3\text{Ph}\cdot\text{SC}_7\text{H}_7$, which crystallises in small needles, melts at 116.5°, is stable towards concentrated hydrochloric acid or fused potassium hydroxide, is oxidised by iodine, and evolves nitrogen with nitrous acid, but does not react with hydrogen sulphide in alcoholic ammoniacal solution. The diacetyl derivative, $\text{C}_{19}\text{H}_{18}\text{ON}_4\text{S}$, forms a white powder, melts at 122°, and is insoluble in acids or aqueous alkalis.

3:5-Dithiol-1-phenyl-1:2:4-triazole, $\begin{array}{c} \text{NHPh}\cdot\text{N} \\ | \\ \text{C}(\text{SH})\cdot\text{N} \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}\cdot\text{SH}$, crystallises

from glacial acetic acid in yellow needles, melts at 193°, is readily soluble in hot water or dilute alkali hydroxides or carbonates, has a strong acid reaction, gives precipitates with the salts of the heavy metals, and is stable towards boiling hydrochloric acid or lead oxide and sodium carbonate. The acetyl derivative crystallises in yellow needles and melts at 284—285°; the dibenzyl ether, $\text{C}_{22}\text{H}_{19}\text{N}_3\text{S}_2$, crystallises in stellate aggregates of needles and melts at 69.5°. When oxidised with iodine in alcoholic solution, the dithioltriazole yields the product, $\text{C}_{16}\text{H}_{10}\text{N}_6\text{S}_4$, which crystallises from glacial acetic acid and melts at 181°.

Anilthiouret, $\text{NHPh}\cdot\text{N}\cdot\text{C} \begin{array}{c} \diagup \text{S} \diagdown \\ \diagdown \text{NH} \diagup \end{array} \text{C}\cdot\text{NH}$, crystallises from dilute hydrochloric acid as a yellow powder, melts at 224—227°, loses

hydrogen sulphide when boiled with lead oxide and aqueous sodium carbonate, and when treated with benzyl chloride and sodium hydroxide is converted into 5-amino-3-thiobenzyl-1-phenyl-1:2:4-triazole, $\text{NH}_2 \cdot \text{C}_2\text{N}_3\text{Ph} \cdot \text{S} \cdot \text{CH}_2\text{Ph}$, which crystallises in thin, glistening leaflets, melts at 137° , and forms a *monoacetyl* derivative, $\text{C}_{15}\text{H}_{13}\text{N}_4\text{S}\text{Ac}$; when condensed with acetone, anilthiouret yields the *product*, $\text{C}_8\text{H}_8\text{N}_4\text{S}_2$, which crystallises from alcohol and melts at 223° .

5-Amino-3-thiol- or 3-amino-5-thiol-1-phenyl-2-methyl-2:3-dihydro-1:2:4-triazole, $\text{C}_9\text{H}_{10}\text{N}_4\text{S}$, formed by the action of *s*-phenylmethylhydrazine on perthiocyanic acid, crystallises in matted, white needles and melts at 213° . G. Y.

New Compound obtained by the Action of Iodine on Benzaldehyde Phenylhydrazone in Pyridine Solution. GIOVANNI ORTOLEVA (*Gazzetta*, 1906, 36, i, 473—476. Compare Abstr., 1904, i, 99).—The compound melting at $265\text{--}267^\circ$, to which the author previously ascribed the formula $\text{C}_{18}\text{H}_{13}\text{N}_3\text{I}$, is now shown to have the formula $\text{C}_{18}\text{H}_{14}\text{N}_3\text{I}$, and to be the hydriodide of a base, $\text{C}_{18}\text{H}_{13}\text{N}_3$, having the constitution $\begin{array}{c} \text{CH} \cdot \text{CH} : \text{C} \cdot \text{CPh} \\ | \qquad \qquad | \\ \text{CH} - \text{N} : \text{C} \cdot \text{NPh} \end{array} \gg \text{N}$.

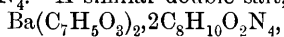
When treated with potassium permanganate, this compound gives a good yield of a new *base*, $\begin{array}{c} \text{CH} \cdot \text{CH} : \text{C} \cdot \text{CPh} \\ | \qquad \qquad | \\ \text{CH} - \text{N} : \text{C} \cdot \text{NH} \end{array} \gg \text{N}$, which crystallises from light petroleum in small, mammillary masses melting at $75\text{--}78^\circ$ and is soluble in most organic solvents. This base yields a picrate and hydrochloride, and gives a white precipitate with silver nitrate or mercuric chloride. The *platinichloride* is red, and is decomposed by boiling water, giving the free base; when heated at $180\text{--}200^\circ$, it loses 4HCl and is transformed into the *platinosochloride*, $(\text{C}_{12}\text{H}_7\text{N}_3)_2\text{PtCl}_4$, which is obtained as a yellow powder. T. H. P.

Preparation of Substituted Diiminobarbituric Acids. EMANUEL MERCK (D.R.-P. 166448).—Malononitrile and its *C*-alkyl derivatives condense with carbamide and its homologues in the presence of the alkali metals or their amides or alkoxides to yield substituted diiminobarbituric acids, which are readily converted into the corresponding barbituric acids; these products are of importance in therapeutics.

4:6-Di-imino-5-oxy-5-diethylpyrimidine was thus obtained from diethylmalononitrile, carbamide, and sodium ethoxide at 100° ; it separates in crystalline aggregates and melts at 277° (corr.); it forms salts with the mineral acids, and is soluble in aqueous alkali hydroxides, but not in ammonia. G. T. M.

Soluble Double Salts of 1:3-Dimethylxanthine and 1:3:7-Trimethylxanthine with Barium Salicylate. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 168293).—When 1 mol. of barium salicylate and 2 mols. of 1:3-dimethylxanthine (theophylline) are mixed in warm water and the solution concentrated under diminished

pressure, a soluble double salt is produced, which has the composition $\text{Ba}(\text{C}_7\text{H}_5\text{O}_3)_2, 2\text{C}_7\text{H}_8\text{O}_2\text{N}_4$. A similar double salt,



is obtained from 1 : 3 : 7-trimethylxanthine.

G. T. M.

Soluble Double Salts of 3:7-Dimethyl-1-ethylxanthine. J. D. RIEDEL (D.R.-P. 170302).—3:7-Dimethyl-1-ethylxanthine in aqueous solution combines with sodium benzoate or salicylate, and with lithium benzoate or salicylate to form soluble double salts, which are obtained either on evaporation or on adding alcohol or acetone.

G. T. M.

[Colouring Matters of the Cyanine Series.] FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 167770).—2:6-Dimethylquinoline-*p*-methoxyquinolinecyanine ethiodide is produced by heating 2:6-dimethylquinoline ethiodide and *p*-methoxyquinoline ethiodide with alcoholic potash; it is precipitated by ether and recrystallised from alcohol, when it separates in lustrous, brown leaflets.

6-Methoxy-2-methylquinoline-6-methylquinolinecyanine methiodide is similarly obtained from the methiodides of 6-methoxy-2-methylquinoline and 6-methylquinoline by the action of potassium hydroxide in methyl-alcoholic solution; it separates in long, green needles. Both these cyanine colouring matters dissolve in alcohol to reddish-violet solutions.

G. T. M.

Azoxy-compounds. ANGELO ANGELI and GUERRIERO MARCHETTI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 480—482).—Treatment of a mixture of aniline and nitrobenzene with sodium yields a salt which ignites spontaneously in the air, the sodium content of which points to the formula $\text{NPhNa} \cdot \text{NPhO} \cdot \text{ONa}$; the salt is readily hydrolysed by water, yielding an appreciable proportion of azoxybenzene. Similarly, the condensation of α -naphthylamine with α -nitronaphthalene gives a compound from which a good yield of α -azoxynaphthalene is obtainable.

The interaction either of aniline and α -nitronaphthalene or of nitrobenzene and α -naphthylamine in presence of sodium yields two isomeric compounds, probably represented by the formulæ $\text{NPh} \cdot \text{NO} \cdot \text{C}_{10}\text{H}_7$ and $\text{NOPh} \cdot \text{N} \cdot \text{C}_{10}\text{H}_7$.

The condensation of the amines with nitro-derivatives in presence of sodium is hence general, the most important cases yet met with being represented by the following equations:

- (1) $\text{OH} \cdot \text{NH}_2 + \text{NO}_2 \cdot \text{C}_6\text{H}_5 = \text{HO} \cdot \text{N}_2\text{O} \cdot \text{C}_6\text{H}_5 + \text{H}_2\text{O}.$
- (2) $\text{OH} \cdot \text{NH}_2 + \text{NO}_2 \cdot \text{OEt} = \text{HO} \cdot \text{N}_2\text{O} \cdot \text{OH} + \text{Et} \cdot \text{OH}.$
- (3) $\text{C}_6\text{H}_5 \cdot \text{NH}_2 + \text{NO}_2 \cdot \text{OEt} = \text{C}_6\text{H}_5 \cdot \text{N}_2\text{O} \cdot \text{OH} + \text{Et} \cdot \text{OH}.$
- (4) $\text{C}_6\text{H}_5 \cdot \text{NH}_2 + \text{NO}_2 \cdot \text{C}_6\text{H}_5 = \text{C}_6\text{H}_5 \cdot \text{N}_2\text{O} \cdot \text{C}_6\text{H}_5 + \text{H}_2\text{O}.$

Each of the reactions (1) and (3) leads to the formation of isomeric products.

T. H. P.

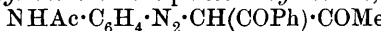
Decomposition of Azo-compounds by Sodium Hyposulphite. EUGÈNE GRANDMOUGIN (*Ber.*, 1906, 39, 2494—2497).—Sodium hyposulphite is a very convenient reducing agent for azo-compounds in boiling aqueous or alcoholic solutions. Azobenzene gives a quantita-

tive yield of hydrazobenzene; α -nitroso- β -naphthol forms α -amino- β -naphthol-4-sulphonic acid (Böniger, Abstr., 1894, i, 199); Orange II, benzeneazo- β -naphthol, and benzeneazo- α -naphthol yield the corresponding aminonaphthols.

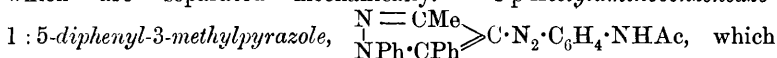
2-Amino- α -naphthol forms a *diacetyl* derivative which crystallises in white needles, melts at 116° , and by partial hydrolysis yields the *N*-acetyl compound, which has been previously described (compare Abstr., 1892, 861). C. S.

[Reduction of Nitroazo-compounds.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D. R.-P. 169826).—5-Nitro-2-amino-*p*-tolyl methyl ether, $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me}(\text{OMe}) \cdot \text{NH}_2$, when diazotised and combined with 7-amino- α -naphthol-3:6-disulphonic acid in alkaline solution, yields a nitroazo-derivative which, when gently warmed with aqueous sodium sulphide, yields an aminoazo-compound giving bluish-black shades on wool in an acid-bath. Other nitroazo-colouring matters are reduced under similar conditions. G. T. M.

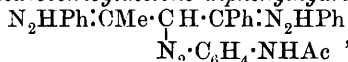
Mixed Disazo-compounds from *p*-Phenylenediamine with Heterocyclic Side-chains. CARL BÜLOW and FRITZ BUSSE (*Ber.*, 1906, 39, 2459—2466).—When benzoylacetone reacts in alcoholic solution with the diazonium compound obtained from acetyl-*p*-phenylenediamine, *p*-acetylaminobenzene-*p*-azobenzoylacetone,



is obtained. It separates from dilute alcohol in golden-yellow needles, melts at 171° , dissolves in dilute alkali to a dark red solution, and is reprecipitated unchanged by carbon dioxide. It reacts with phenylhydrazine in boiling glacial acetic acid to form two products which are separated mechanically. 4-*p*-Acetylaminobenzeneazo-

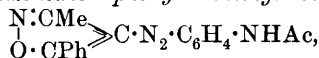


forms orange-red crystals, melts and decomposes at 229° and is insoluble in dilute alkalis. The main product of the reaction is *p*-acetylaminobenzeneazobenzoylacetone diphenylhydrazone,



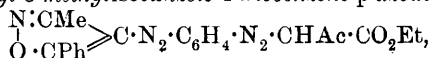
which crystallises in yellow needles and melts at 206° .

4-*p*-Acetylaminobenzeneazo-5-phenyl-3-methylisooxazole,



obtained from acetylaminobenzeneazobenzoylacetone and hydroxylamine in boiling alcoholic solution, separates from alcohol in large, yellow needles, melts and decomposes at 228° , and develops a red coloration with concentrated sulphuric acid. By hydrolysis with alcohol and 10 per cent. sodium hydroxide, 4-*p*-aminobenzeneazo-5-phenyl-3-methylisooxazole, $\text{C}_{16}\text{H}_{14}\text{ON}_4$, is obtained, which separates from alcohol in reddish-yellow, glistening needles and melts at 191° .

Ethyl 5-phenyl-3-methylisooxazole-4-azobenzene-*p*-azoacetoacetate,



obtained from an alcoholic solution of ethyl acetoacetate and the diazonium salt derived from the preceding compound, in the presence of sodium acetate, forms micro-crystalline, orange needles, melts at 151° , and dissolves in hot dilute alkalis with the loss of carbon dioxide.

5-Phenyl-3-methylisooxazole-4-azobenzene-p-4'-azo-1'-phenyl-3'-methyl-5'-pyrazolone, $\begin{array}{c} \text{N}:\text{CMe} \\ | \\ \text{O} \cdot \text{CPh} \end{array} \gg \text{C} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{CH} < \begin{array}{c} \text{CMe}:\text{N} \\ | \\ \text{CO}-\text{NPh} \end{array}$, is obtained

when phenylhydrazine is slowly added to a glacial acetic acid solution of the preceding compound. It separates from its solution in nitrobenzene after the addition of alcohol or glacial acetic acid in red needles, melts and decomposes at $205-206^{\circ}$, dissolves in concentrated sulphuric acid to a reddish-violet solution, but is insoluble in hydrochloric acid or in a solution of sodium hydroxide.

The constitution of this compound has been confirmed by its formation in the reverse order by the following changes: 4-*p*-aminobenzene-azo-1-phenyl-3-methyl-5-pyrazolone (compare Abstr., 1900, i, 261) \rightarrow 1-phenyl-3-methyl-5-pyrazolone-4-azobenzene-p-4'-azobenzoylacetone, which melts and decomposes at $231-232^{\circ}$, \rightarrow 1-phenyl-3-methyl-5-pyrazolone-4-azobenzene-p-4'-azo-3'-phenyl-5'-methylisooxazole, which is identical with the compound previously described. C. S.

[The Diazotisation of Substituted Meta-diamines.] GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 168299).—2:4-Diaminophenol-6-carboxylic or -sulphonic acid can be readily diazotised to a bisdiazonium salt. Tolylene-2:4-diamine and 4-chloro-*m*-phenylenediamine, on the other hand, do not diazotise readily, for the diazonium salt first formed combines with the still undiazotised diamine to form azo-compounds of the type of Bismarck brown. 2:4-Diaminophenol, which might also be expected to yield azo-derivatives by this secondary reaction, is found, however, to diazotise quite readily in the presence of sufficient mineral acid. The solution of the bisdiazonium salt has a reddish-yellow colour, and the compound combines with the α -naphtholsulphonic acids (5 and 6), even in acetic acid solutions, to yield an intermediate azodiazoproduct, which in alkaline solutions condenses further with a phenol or phenolsulphonic acid to give rise to a tetrazo-colouring matter. G. T. M.

Occurrence of Glycyl-proline Anhydride in the Tryptic Decomposition Products of Gelatin. PHOEBUS A. LEVENE and WALLACE A. BEATTY (*Ber.*, 1906, 39, 2060—2061).—The compound $\text{C}_7\text{H}_{10}\text{O}_2\text{N}_2$, described previously (this vol., i, 469), is readily hydrolysed when heated at 150° with concentrated hydrochloric acid. The products obtained are α -proline [pyrrolidine-2-carboxylic acid] and glycine, and the original substance thus appears to be glycyl-proline anhydride.

J. J. S.

Formation of Dipeptides by the Hydrolysis of Proteids. EMIL FISCHER and EMIL ABDERHALDEN (*Ber.*, 1906, 39, 2315—2320. Compare this vol., i, 326; Levene and Beatty, preceding abstract).—Detailed instructions are given for the isolation of glycyl-l-tyrosine

anhydride, $C_{11}H_{12}O_3N_2$, from the products of the hydrolysis of silk-fibroin by hydrochloric acid. It separates from hot water in a felted mass of colourless needles, melts and decomposes at $278-283^\circ$ (corr.), is hydrolysed by 25 per cent. sulphuric acid to tyrosine and glycine, and is identical with the synthetic product in crystalline form, melting point, and solubility, but differs slightly in rotatory power, $[\alpha]_D$ at 20° being 123.3° as against 126.4° .

Glycyl-L-leucine anhydride, $C_8H_{14}O_2N_2$, has been isolated from the products of hydrolysis of elastin by 70 per cent. sulphuric acid; it separates slowly from hot alcohol or acetone in microscopic needles, melts at 253° (corr.), has $[\alpha]_D$ 29.2° at 20° , is hydrolysed by concentrated hydrochloric acid at 100° to glycine and leucine, and is identical with the synthetically prepared anhydride. C. S.

The True Nature of the "Leucines" and "Glucoproteins" obtained by Schützenberger in the Decomposition of Proteid Matter. LOUIS HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1906, 142, 1426—1428).—By fractional precipitation by means of phosphotungstic acid, Schützenberger's leucines, "leuceines," and "glucoproteins" (Abstr., 1877, i, 725; 1879, 542) can be separated into well-known amino-acids; thus, the leucine group $C_nH_{2n+1}O_2N$ contains 10 per cent. of alanine, 41 per cent. of leucine, 2.8 per cent. of phenylalanine, 1 per cent. of aspartic acid, 0.8 per cent. of glutamic acid, and 5 per cent. of tyrosine; the leucine group $C_nH_{2n-1}O_2N$ contains 0.27 per cent. of tyrosine, 21 per cent. of alanine, 31 per cent. of leucine, 5.8 per cent. of proline, 19 per cent. of phenylalanine, 3.9 per cent. of aspartic acid, and 1.9 per cent. of glutamic acid; and the glucoprotein group, $C_nH_{2n}O_4N$, contains 13 per cent. of alanine, 12 per cent. of leucine, 0.2 per cent. of proline, 7 per cent. of phenylalanine, 5 per cent. of aspartic acid, and 12 per cent. of glutamic acid. M. A. W.

The "Chlorination" of Wool. LÉO VIGNON and J. MOLLARD (*Compt. rend.*, 1906, 142, 1343—1345).—The authors have examined the action of gaseous chlorine, chlorine water, and bleaching powder, in acid solution on wool, and find that whilst it is dissolved by the prolonged action of the gas, its properties are modified when the action is limited, and it loses 10 per cent. of its weight, is dyed more readily, giving deeper and more brilliant tints, and becomes unshrinkable. The chlorine is not fixed by the wool, but it appears to destroy the projecting points (hooks) of the scales, and thus diminish its aptitude for felting and shrinking; at the same time the increase in the acid and basic functions caused by the rupture of certain linkings of amino-acids would account for the increase in the tinctorial properties. M. A. W.

Compounds of Nucleic Acid and Proteid, with Special Reference to those in the Mammary Gland and their Relation to Caseinogen Formation. WILHELM LÖBISCH (*Beitr. chem. Physiol. Path.*, 1906, 8, 191—209).—Nucleic acid from the mammary gland in its composition and properties is closely related to the

nucleic acids from the thymus and spermatozoa, and not to guanylic acid. It yields a carbohydrate group. The hypothesis that caseinogen is a simple compound of this acid with the serum proteid is not tenable. The reason for this view and the general theoretical conceptions of the way in which nucleic acid can unite with proteids are discussed.

W. D. H.

Crystalline Chitosan Compounds from Sepia Shells. OTTO VON FÜRTH and MICHELE RUSSO (*Beitr. chem. Physiol. Path.*, 1906, 8, 163—190).—Chitosan hydrochloride and hydrobromide can be obtained in characteristic crystalline form. Araki's formula, $C_{14}H_{26}O_{10}N_2$, for chitosan is disputed; the molecule is at least twice, perhaps four times, heavier. It contains neither aldehyde nor carboxyl groups, and its nitrogen has the character of a secondary amine. It can combine with one molecule of hydrochloric acid for each atom of nitrogen; the compound is a loose one, and some of the acid is removable in a vacuum. On decomposition with acids, the hydrochloride yields acetic acid 25 and glucosamine 60 per cent. All the glucosamine complexes appear to be acetylated. It takes up one benzoyl group per nitrogen atom. A large part of the oxygen in the molecule is present in hydroxylic form. Chitosan gives with bromine a scarlet additive product from which the bromine is removed by warming with water. The chitosans obtained from the skeletal substance of arthropods and molluscs are identical. The integuments of butterfly pupæ are made of chitin, not of Griffiths' pupin.

W. D. H.

Action of Light on Enzymes in Oxygen and in Hydrogen, compared with the Action of Photodynamic Substances. A. JODLBAUER and HERMANN VON TAPPEINER (*Chem. Centr.*, 1906, i, 487; from *Arch. Klin. Med.*, 85, 386—394).—Fluorescent substances, even with intense light, only act in presence of oxygen. Sunlight, deprived of ultra-violet rays, will alone injure invertin when oxygen is present. It is probable that photodynamic action consists in a quickening of the simple action of light. This quickening action is very considerable. The effect of sunlight and eosin in concentrations of $N/2000$ (optimum) in ten minutes was four times as great as that of sunlight, free from ultra-violet rays, in fifteen minutes.

N. H. J. M.

The Supposed Identity of Pepsin and Rennin. SIGVAL SCHMIDT-NIELSEN (*Zeit. physiol. Chem.*, 1906, 48, 92—109).—The conclusion is drawn that the enzyme which curdles neutral milk cannot be identical with pepsin.

W. D. H.

Organic Chemistry.

Reactions of Acetylene with Acidified Solutions of Mercury and Silver Salts. JULIUS A. NIEUWLAND and J. A. MAGUIRE (*J. Amer. Chem. Soc.*, 1906, 28, 1025—1031. Compare Nieuwland, *Abstr.*, 1905, i, 557; Poleck and Thummel, *Abstr.*, 1890, 118; Hofmann, *Abstr.*, 1905, i, 268).—When passed into a solution of mercuric chromate in aqueous chromic acid, acetylene forms a bright yellow *precipitate*, $\text{CrO}_4\text{Hg}_2\text{C}\begin{smallmatrix} \text{C}\cdot\text{OH} \\ \text{CH} \end{smallmatrix}$, which becomes brown when dried,

forms iodoform with moist iodine, especially in alkaline solution, deflagrates, forming carbon and chromium oxide, when rubbed in a mortar or touched with a hot glass rod, and dissolves in presence of nascent chlorine. With mercuric silicofluoride, acetylene forms a white *precipitate* which turns blue, has an odour of aldehyde, decomposes even when dry, gives the iodoform reaction, reacts energetically with dry bromine or chlorine, and is decomposed by concentrated hydrochloric acid. A similar *precipitate* is formed by the action of acetylene on mercuric fluoroborate.

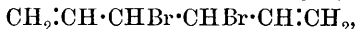
The white *precipitate* obtained on passing acetylene into a solution of mercuric chlorate in chloric acid is extremely explosive when rubbed, on percussion, or on contact with sulphuric acid, yields acetaldehyde in contact with water, and gives the iodoform reaction in alkaline solution; it decomposes only slowly when moist, attacks organic matter such as paper, and is soluble in acids. A similar *precipitate* is formed with mercuric perchlorate; when pure this is not exploded by heat, friction, or treatment with sulphuric acid. Acetylene and mercuric nitrite interact with development of heat, forming a heavy, cream-coloured *precipitate*, $\text{C}_2(\text{HgNO}_2)_2$, which decomposes when heated and gives the iodoform reaction in alkaline solution. Similar white *precipitates* are formed by acetylene with mercury acetamide and mercuric bromate.

Acetylene forms explosive *precipitates* with silver fluoride, nitrite, silicofluoride, fluoroborate, and bromate in acid solutions and with silver chloride in sodium hyposulphite solution. The *precipitate*, $3\text{C}_2\text{H}_2\cdot 2\text{H}_3\text{PO}_4\cdot \text{Ag}_3\text{PO}_4\cdot \text{H}_2\text{O}$, formed from acetylene and silver phosphate in acid solution, is stable, swells and decomposes when heated, is only slowly decomposed when acted on by light, and dissolves in potassium cyanide solution, liberating acetylene. Acetylene does not form *precipitates* with silver chromate or cyanide, but with silver perchlorate it yields an extremely explosive *compound* which is dangerous to prepare even in the smallest quantity. These compounds of silver and acetylene do not give the iodoform reaction, and with the exception of the phosphate are rapidly blackened on exposure to light.

(G. Y.)

Derivatives of $\alpha\gamma$ -Hexatriene. PIETER VAN ROMBURGH and W. VAN DORSSEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 111—115. Compare this vol., i, 130, 141).—A new preparation of the hydrocarbon, $\text{CH}_2\text{:CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2$ (by heating the formate of *s*-divinyl glycol), which was purified by fractionation from sodium and finally distilling in an atmosphere of carbon dioxide, boiled at $77\text{--}78.5^\circ$ under a pressure of 764.4 mm.; it had a sp. gr. 0.749 and $n_D 1.4884$ at 13.5° .

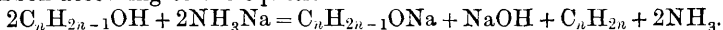
When treated with bromine at -10° , the dibromide, $\text{C}_6\text{H}_8\text{Br}_2$, is obtained as colourless crystals melting at $85.5\text{--}86^\circ$; at higher temperatures a tetrabromide, $\text{C}_6\text{H}_8\text{Br}_4$, is obtained, melting at $114\text{--}115^\circ$; at the same time a hexabromide, $\text{C}_6\text{H}_8\text{Br}_6$, is always produced, and can be separated by ethyl acetate, and melts at $163.5\text{--}164^\circ$. The dibromide and tetrabromide are identical with compounds obtained by Griner by the action of phosphorus tribromide on *s*-divinyl glycol. These facts show that the dibromide has the constitution



and that the addition of the bromine to the hexadiene has not followed Thiele's rule.

When reduced with hydrogen at $125\text{--}130^\circ$ in the presence of nickel, *n*-hexane is formed. When the hexatriene is reduced with sodium and alcohol, a mixture of hexene and a hexadiene is obtained which could not be resolved into its constituents. It is suggested that the reduction has followed two courses: first a mixture of two hexadienes, the $\beta\delta$, $\text{CHMe}\text{:CH}\cdot\text{CH}\cdot\text{CHMe}$, and the $\beta\epsilon$, $\text{CHMe}\text{:CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$, is produced; the former alone can be further reduced by this method, yielding γ -hexene, $\text{CH}_2\text{Me}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\text{Me}$. K. J. P. O.

Reduction of Unsaturated Primary Alcohols of the Fatty Series by Metal-ammonium Compounds. E. CHABLAY (*Compt. rend.*, 1906, 143, 123—126. Compare Abstr., 1905, i, 502).—The unsaturated primary alcohols of the fatty series react with metal-ammonium compounds to form the corresponding unsaturated hydrocarbon according to the equation



From allyl alcohol, propylene is thus obtained in quantitative yield. The reaction is extremely energetic and is best conducted by allowing the alcohol to fall drop by drop into the solution of the metal-ammonium compound at -40° . The reaction has also been tried with citronellol, which yields a hydrocarbon boiling at $168\text{--}169^\circ$ under 760 mm. pressure. It has a sp. gr. 0.789 at 0° , 0.777 at 22.5° , $n_D = 1.4484$ at 22.6° . It is probably $\text{CMe}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_3$, but a small quantity only has been obtained.

It is to be noted that sodium gives both hydrogen and propylene with allyl alcohol, whereas sodammonium yields only the hydrocarbon.

H. M. D.

Determination of the Molecular Weights of Alcohols and of Phenols by the Use of Benzoic Anhydride. ALBERT GASCARD (*J. Pharm. Chim.*, 1906, [vi], 24, 97—101).—When an alcohol or phenol is esterified by means of benzoic anhydride, one molecule of

benzoic acid is formed for each molecule of alcohol or phenol originally taken, according to the equation $R\cdot OH + (COPh)_2O = Ph\cdot CO_2R + Ph\cdot CO_2H$, and the molecular weight of the alcohol or phenol can therefore be determined by estimating the benzoic acid present in the resulting mixture. The method of procedure is as follows: about half a gram of the pure alcohol or phenol is placed in a long-necked flask together with two or three times the calculated quantity of benzoic anhydride, the flask is sealed and heated for about twenty-four hours by complete immersion in a bath of water, saturated solution of calcium chloride, or oil, according to the temperature required to complete the esterification; the flask is cooled and opened, and 10 to 20 c.c. pure ether, benzene, or chloroform added to dissolve the mixture of ester, anhydride, and acid; 5 c.c. of water are then added and the acid titrated by means of normal potassium carbonate in the presence of phenolphthalein; the molecular weight (P) of the alcohol is given by the equation $P = p \times 1000/N$, where p is the weight of alcohol taken and N is the number of c.c. of alkali employed. As benzoic anhydride usually contains a little free benzoic acid it is advisable to make a blank experiment to determine the amount; but control experiments show that neither benzoic anhydride nor the ester of a primary or secondary alcohol is appreciably hydrolysed under the conditions of the experiment.

M. A. W.

Boiling Points of some Secondary and Tertiary Alcohols.

GUSTAV D. HINRICHS (*Compt. rend.*, 1906, 143, 359—361).—The author has previously shown (this Journal, 1873, 1014) that the boiling point of a compound is a function of its maximum moment of inertia; the secondary and tertiary alcohols, $C_nH_{2n+1}OH$, examined by Henry (following abstract), afford a further illustration of this generalisation; their maximum moments of inertia are given below, and the order is the same as that observed by Henry in their boiling points.

For n .	5.	6.	7.	8.	9.
Tertiary alcohol.....	79	168	309	501	746
Secondary alcohol	82	161	286	468	712

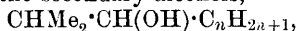
M. A. W.

Secondary Alcohols from the Octane, $CHMe_2\cdot[CH_2]_4\cdot CH_3$.

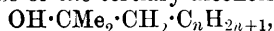
LOUIS HENRY [with BUELENS and MUSSET] (*Compt. rend.*, 1906, 143, 102—104).—Whilst the secondary alcohols derived from normal octane have approximately the same boiling point, it is found that the boiling points of the various secondary alcohols derived from the β -methyloctane, $CHMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3$, differ considerably. The boiling rises regularly as the distance of the carbinol group from the carbon atom to which the two methyl groups are attached increases. The respective boiling points are γ 153—154°, δ 160—161°, ϵ 165—166°, ζ 171—172°.

When the γ -alcohol is converted into the corresponding halogen compound and this is hydrolysed, the tertiary dimethylpentylcarbinol,

$C_5H_{11} \cdot CMe_2 \cdot OH$, is obtained, and this boils at 162° , which is considerably higher than the boiling point of the secondary γ -alcohol. If the boiling points of the secondary alcohols,



are compared with those of the tertiary alcohols,



it is found that the relationship between the boiling points changes as the number of carbon atoms in the molecule increases. In the case of pentane and hexane the secondary alcohol boils 10° and 6° respectively above the tertiary alcohol; the alcohols derived from heptane have the same boiling point, whilst in the case of octane the tertiary alcohol boils 8° higher than the corresponding secondary compound.

H. M. D.

Transformation of Secondary-tertiary α -Glycols into Ketones and the Transposition of Hydrobenzoin. MARC TIFFENEAU and DORLENCOURT (*Compt. rend.*, 1906, 143, 126—128).— γ -Ethylpentylene $\beta\gamma$ -glycol, obtained by the action of magnesium ethyl bromide on ethyl lactate, boils at 194 — 197° under the ordinary pressure and has a sp. gr. 0.957 at 20° . When heated with sulphuric acid it yields diethylacetone. *aa*-Diphenylpropylene $\alpha\beta$ -glycol melts at 96° , and in the same way yields diphenylacetone melting at 45 — 47° , which gives a semicarbazone of melting point 165 — 166° .

α -Phenyl- β -ethylbutylene $\alpha\beta$ -glycol, which melts at 89° , is converted by sulphuric acid into phenyl isopentyl ketone, $C_6H_5 \cdot CO \cdot CHEt_2$. This boils at 230 — 236° and yields a semicarbazone melting at 179° .

Methylhydrobenzoin, melting at 104° , is converted into methyl deoxybenzoin, which boils at 193° under 25 mm. pressure and gives a semicarbazone melting at 194° .

In the same way ethylhydrobenzoin, melting at 117° , yields ethyldeoxybenzoin, the semicarbazone of which melts at 167° .

These changes are quite analogous to the formation of diethylacetone and diphenylacetone from ethylpentylene glycol and diphenylpropylene glycol respectively, and the intramolecular transposition which takes place in the formation of diphenylacetaldehyde from hydrobenzoin is quite exceptional. The phenomenon of dehydration in the case of glycols of the type $ArCH(OH) \cdot CH(OH)Ar'$ is therefore different from that of glycols of the general formula $ArRC(OH) \cdot CH(OH)Ar'$.

H. M. D.

Rectification of Official Ethyl Ether. P. GUIGUES (*J. Pharm. Chim.*, 1906, [vi], 24, 204).—Ethyl ether containing alcohol can be conveniently purified by distillation over colophony, which retains the alcohol. Five per cent. of 98 per cent. alcohol was added to pure anhydrous ether having a sp. gr. 0.720 at 15° , the sp. gr. of the mixture after drying over anhydrous potassium carbonate was 0.725, and this fell to 0.721 after once washing with water; the ether, still retaining 1 per cent. of alcohol, was placed in contact with colophony (50 grams per litre of ether), and finally distilled; the distillate was pure ethyl ether having a sp. gr. 0.720 at 15° .

M. A. W.

Triformin (Glyceryl Triformate). PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 109—111).—Although diformin is produced as an intermediate product in the preparation of formic acid from oxalic acid and glycerol, it is difficult to demonstrate the presence of triformin. When a large excess of anhydrous oxalic acid is used and the product distilled under reduced pressure, an oil is obtained which has a sp. gr. 1.309 at 25°, and by titration is shown to consist of 90 per cent. of triformin. Similar results are obtained when pure diformin is treated with anhydrous formic acid. The triformin may be isolated from these mixtures by cooling the oil with liquid ammonia, when crystals separate, which can be freed from liquid. Triformin crystallises in needles melting at 18°, and as a liquid has a sp. gr. 1.320 and n_D 1.4412 at 18°; it boils at 163° under 38 mm. and at 266° under the ordinary pressure. If mixed with diformin, distillation at the ordinary pressure is accompanied by decomposition, carbon monoxide and dioxide being evolved and allyl formate distilling over. On very slow distillation at the ordinary pressure, triformin decomposes into allyl formate, formic acid, and allyl alcohol, which distil, and glycerol which remains in the residue, the oxides of carbon being at the same time evolved.

Triformin is hydrolysed slowly by cold water, but more rapidly by warm water. It reacts with ammonia and amines, yielding the corresponding formamide and glycerol.

K. J. P. O.

The Fatty Acids of Kephalin. H. COUSIN (*J. Pharm. Chim.*, 1906, [vi], 24, 101—108. Compare Koch, this vol., ii, 136).—Kephalin, precipitated by alcohol from an ethereal extract of dried ox's brain and purified by repeated treatment with boiling alcohol, forms a firm, waxy, pale yellow mass, becoming reddish-brown with time; it is insoluble in water or acetone, slightly soluble in ethyl acetate or cold alcohol, soluble in hot alcohol; it contains from 3.73 to 3.89 per cent. of phosphorus and 1.82 to 1.86 per cent. of nitrogen, which correspond with the ratios P:N = 2.0 to 2.12. The nitrogen bases were removed by partial hydrolysis by heating with a dilute hydrochloric acid, and the residual mixture of fatty acids and glycerophosphoric esters completely saponified by prolonged boiling with an alcoholic solution of potassium hydroxide in alcohol. The glycerophosphoric acid was isolated in the form of its calcium salt, and the mixture of fatty acids, having an iodine value 96 to 102, was separated according to the method previously employed in the case of lecithin (*Abstr.*, 1903, i, 675; this vol., i, 330) into unsaturated and saturated acids. The unsaturated acid or acids (Thudichum's "kephalic acid") is either linoleic acid or a mixture of acids belonging to this series, and stearic acid is the only saturated acid.

M. A. W.

Constitution of Phenylangelicalactone and isoOctenelactone. JOHANNES THIELE and WILHELM WEDEMANN (*Annalen*, 1906, 347, 132—142).—It has been shown by Fittig that both the Δ^1 and Δ^2 crotonolactones yield the same γ -ketonic acid. Two such lactones, phenylangelicalactone and iso-octenelactone, have been here demonstrated to have the Δ^1 constitution.

When phenylangelicalactone, $\text{CH}_2\text{Ph}\cdot\text{CH}\langle\begin{smallmatrix}\text{CH} \\ \text{O}\cdot\text{CO}\end{smallmatrix}\rangle\text{CH}$, is oxidised with permanganate in neutral alcoholic solution, *phenyldihydroxyvalerolactone*, $\text{CH}_2\text{Ph}\cdot\text{CH}\langle\begin{smallmatrix}\text{CH}(\text{OH}) \\ \text{O}\text{---}\text{CO}\end{smallmatrix}\rangle\text{CH}\cdot\text{OH}$, is obtained, crystallising in needles melting at 124° . With acetyl chloride, it yields a *diacetyl* derivative, $\text{C}_{15}\text{H}_{16}\text{O}_6$, as a thick oil, and with *p*-nitrobenzoyl chloride, a *p*-nitrobenzoate, $\text{C}_{25}\text{H}_{18}\text{O}_{10}\text{N}_2$, which crystallises in needles melting at 130° . On hydrolysis with barium hydroxide, the barium salt of trihydroxyphenylvaleric acid is formed; the *silver* salt is an amorphous precipitate.

*iso*Octenelactone, $\text{CH}_2\text{Pr}^\beta\cdot\text{CH}\langle\begin{smallmatrix}\text{CH} \\ \text{O}\cdot\text{CO}\end{smallmatrix}\rangle\text{CH}$, is prepared by the action of anhydrous sodium acetate on $\beta\gamma$ -dibromo*isooctenoic* acid, and is an oil of pleasant odour. When oxidised, it yields $\alpha\beta$ -*dihydroxy-γ-isobutylbutyrolactone*, $\text{CH}_2\text{Pr}^\beta\cdot\text{CH}\langle\begin{smallmatrix}\text{CH}(\text{OH}) \\ \text{O}\text{---}\text{CO}\end{smallmatrix}\rangle\text{CH}\cdot\text{OH}$, which crystallises in needles melting at 124° . The *di-p*-nitrobenzoate, $\text{C}_{22}\text{H}_{20}\text{O}_{10}\text{N}_2$, melts at 147° . On hydrolysis, it yields $\alpha\beta\gamma$ -trihydroxy- γ -isobutylbutyric acid, the *silver* salt of which was analysed. K. J. P. O.

Reactions between Acid Chlorides and Potassium Ethylxanthate. OSWIN W. WILLCOX (*J. Amer. Chem. Soc.*, 1906, 28, 1031—1034).—The action of acetyl chloride on potassium ethylxanthate in cooled dilute ethereal solution leads to the formation of the mixed *anhydride*, $\text{OEt}\cdot\text{CS}\cdot\text{SAc}$, which is obtained as an unstable oil, decomposing when heated into ethyl acetate, carbon disulphide, and other products. In presence of a small amount of ether and without cooling, the action leads to the formation of ethylxanthic anhydride. Only a small amount of this could be obtained from the product of the action of ethyl chlorocarbonate on potassium ethylxanthate.

Ethyl pentathiotricarbonate, $\text{CS}(\text{S}\cdot\text{CS}\cdot\text{OEt})_2$, is formed by the action of thiocarbonyl chloride on potassium ethylxanthate in ice-cooled aqueous solution, or together with a yellowish-brown oil in acetone solution; it separates from benzene in white, microscopic crystals, melts and decomposes at 160° , and is stable towards dilute acids or alkali hydroxides, but is decomposed, depositing sulphur, when heated with concentrated sulphuric acid.

Large amounts of ethylxanthic anhydride are isolated from the product of the action of carbonyl chloride on potassium ethylxanthate in toluene solution. G. Y.

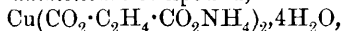
***iso*Succinic Acid.** RICHARD MEYER and PAUL BOCK (*Annalen*, 1906, 347, 93—105).—The preparation of ethyl *isosuccinate* from ethyl γ -bromopropionate and potassium cyanide is unsatisfactory. Attempts to employ Grignard's reaction by treating ethyl γ -bromopropionate successively with magnesium and carbon dioxide were unsuccessful. It was found that the purification of the product of the malonic ester synthesis by conversion of the impure ethyl *isosuccinate* into the crystallisable amide afforded the best results.

Benzyl isosuccinate is an oil; the *p*-nitrobenzyl ester, prepared from

impure silver *isosuccinate* and *p*-nitrobenzyl iodide, crystallises in six-sided plates melting at 75° , but cannot be readily converted into *isosuccinic acid*. The *anilide* of *isosuccinic acid* is obtained by heating the ester with aniline, and crystallises in needles melting at 180 — 181° .

isoSuccinamide is easily hydrolysed by boiling with dilute aqueous sodium hydroxide. The acid, which crystallises in white needles, melts at 127 — 130° and forms a 50.61 — 50.87 per cent. solution in water at 15° . Its molecular heat of combustion was found to be 365.3 Cal. (constant volume), a number in near agreement with Stohmann's value.

Cadmium *isosuccinate* crystallises with H_2O in sparingly soluble needles. The *cupro-ammonium* compound,



prepared from ammonium *isosuccinate* and copper acetate, forms bluish-green crystals. *isoSuccinyl chloride*, prepared from thionyl chloride and *isosuccinic acid* or, better, sodium *isosuccinate*, is a liquid boiling at 75° under 50 mm. pressure. Bromo*isosuccinic acid*, prepared from the pure *isosuccinic acid*, forms large, transparent crystals, apparently octohedral, and melts and decomposes at 165 — 170° .

K. J. P. O.

Esterification of Unsymmetrical Di- and Poly-basic Acids.

XIV. *i*-Aspartic Acid. RUDOLF WEGSCHEIDER and ERICH FRANKL (*Monatsh.*, 1906, 27, 487—501. Compare Wegscheider, this vol., ii, 77).—As stated by Piutti (Abstr., 1888, 677; 1889, 383), the esterification of *i*-aspartic acid by means of alcohol and hydrogen chloride leads to the formation of β -ethyl hydrogen *i*-aspartate, together with traces of the diethyl ester (compare Curtius and Koch, Abstr., 1885, 885; Fischer, Abstr., 1901, i, 192).

The action of silver nitrate on ammonium *i*-aspartate in aqueous solution leads to the formation of the salt, $C_4H_6O_7 \cdot N_2Ag_2$. A salt of approximately the constitution $C_4H_5O_4NaAg_2$ is obtained in presence of an excess of ammonia; when treated with ethyl iodide, this yields ethyl *i*-aspartate, together with small amounts of an *N*-ethylated product.

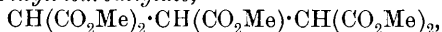
The hydrolysis of the diethyl ester by means of a limited amount of alcoholic potassium hydroxide leads to the formation of a mixture of the diethyl ester and *i*-aspartic acid. No ester was obtained on heating potassium hydrogen *i*-aspartate with ethyl iodide and alcohol at 100° . When heated with alcohol in a sealed tube at 93° , *i*-aspartic acid remains unchanged, but at 150 — 160° it is partially decomposed, yielding carbon dioxide and an oil from which a product could not be isolated.

G. Y.

Transformations of Methyl Dicarboxyaconitate. RICHARD ANSCHÜTZ and ALPHONS DESCHAUER (*Annalen*, 1906, 347, 1—16).—Methyl dicarboxyaconitate is best prepared from methyl dichloro-oxalate (1 mol.) and methyl sodiomalonate (3 mols.), when the following reaction takes place: $OMe \cdot CCl_2 \cdot CO_2Me + 2CHNa(CO_2Me)_2 = 2NaCl + MeOH + C(CO_2Me)_2 \cdot C(CO_2Me) \cdot CH(CO_2Me)_2$. The sodium salt of the methyl dicarboxyaconitate is then formed by interaction

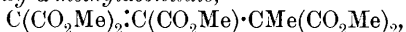
with 1 mol. of methyl sodiomalonate. The ester is purified by recrystallisation from water, and melts at 62°. At the same time, *methyl ethylenetricarboxylate*, $\text{CH}(\text{CO}_2\text{Me})\cdot\text{C}(\text{CO}_2\text{Me})_2$, is formed as a by-product; it crystallises from methyl alcohol, melts at 134—135°, and does not give a yellow coloration with alkalis as does the aconitate.

Methyl dicarboxytricarballylate,



is prepared by reducing methyl dicarboxyaconitate with zinc dust in acetic acid solution, and forms plates melting at 85—86°. It is completely soluble in alkalis and forms the *monosodium* derivative, $\text{C}_{13}\text{H}_{17}\text{O}_{10}\text{Na}$. It may also be prepared from methyl dichloroacetate and methyl sodiomalonate. When boiled with concentrated hydrochloric acid it is quantitatively converted into tricarballic acid melting at 158°.

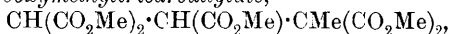
The sodium derivative of methyl dicarboxyaconitate forms small, orange-yellow crystals, and when pure yields with methyl iodide *methyl α-dicarboxy-α-methylaconitate*,



which crystallises in needles, melts at 86°, and boils at 208—210° under 12 mm. pressure.

α-Methylaconitic acid, $\text{CH}(\text{CO}_2\text{H})\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, is prepared by heating methyl dicarboxymethylaconitate with 25 per cent. sodium hydroxide at 60—70° and then isolating the methylaconitic acid as the silver salt; it forms small crystals melting and decomposing at 169—172°. The *silver* salt is a white powder.

Methyl dicarboxymethyltricarballylate,



is obtained by reducing methyl dicarboxymethylaconitate with zinc dust in acetic acid solution, and forms large, transparent crystals melting at 58—59.5°; its *sodium* derivative, $\text{C}_{14}\text{H}_{19}\text{O}_{10}\text{Na}$, is obtained as a solid by adding dry benzene to its methyl-alcoholic solution. When methyl dicarboxymethylaconitate is boiled with 20 per cent. hydrochloric acid, it is converted into a mixture of two *α-methyltricarballic acids*, $\text{CH}_2(\text{CO}_2\text{H})\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, which are separated by crystallisation from water. The sparingly soluble acid melts at 178—180°, whilst the more soluble acid melts at 132—134°. The *silver* salt of each acid was prepared, and the acids proved to be identical with those obtained by Auwers, Köbner, and Meyenberg (*Abstr.*, 1892, i, 41). K. J. P. O.

Synthetical Crystalline *l*-Iditol. GABRIEL BERTRAND and A. LANZENBERG (*Compt. rend.*, 1906, 143, 291—294).—The authors have obtained 28 grams of pure recrystallised *l*-iditol from 300 grams of xylose by the following modification of Fischer and Fay's method (*Abstr.*, 1895, i, 650); the xylose is converted into a mixture of *l*-gulonic and *l*-idonic acids, the latter removed by crystallisation of its lactone, when the mother liquor reduced by sodium amalgam contains *l*-iditol together with a little *l*-sorbitol, which is removed in the form of its benzylidene derivative, and the crystallisation of the *l*-iditol induced by sowing with a crystal of sorbieritol (*α*-iditol) (compare

Maquenne and Bertrand, *Abstr.*, 1901, i, 497). *l*-Iditol crystallises in rhombic prisms, melts at 73.5° , and has $[\alpha]_D + 3.5^{\circ}$ in 10 per cent. aqueous solution at 20° [the corresponding constants of α -iditol are 73.5° and -3.5° respectively, and not 75° and -3.53° as originally stated (compare *Abstr.*, 1905, i, 21)]; the *hexa-acetyl* derivative crystallises in hexagonal plates, melts at 121.5° , and has $[\alpha]_D + 25.33^{\circ}$ in 5 per cent. chloroform solution at 20° [the *hexa-acetyl* derivative of α -iditol melts at 121.5° and has $[\alpha]_D - 25.65^{\circ}$ in 5 per cent. chloroform solution (compare *Abstr.*, 1905, i, 21)]; trimethylene-*l*-iditol crystallises in thin, brilliant needles almost insoluble in alcohol, insoluble in chloroform, soluble in acetic acid, and has $[\alpha]_D - 30^{\circ}$, and not $+8^{\circ}$ as stated by Lobry de Bruyn and Alberda van Eckenstein (*Abstr.*, 1900, i, 332).
M. A. W.

Action of Ammonium Chloride on Aqueous Sucrose Solutions. FRIEDRICH STROHMER and O. FALLADA (*Chem. Centr.*, 1906, i, 1819; from *Österr.-ung. Zeit. Zucker-Ind. Landw.*, 35, 168—171).—On heating in various ways aqueous solutions containing sucrose and ammonium chloride in the proportion 3 : 1 or 1 : 1, it is found that the polarisation diminishes to a greater or less extent, the liquid becoming coloured and capable of reducing Fehling's solution. The solution remains neutral, except when heated at 115° , in which case it becomes faintly acid. Assuming that the solution contains invert sugar, Clerget's formula indicates an amount of this sugar corresponding very nearly with the original proportion of sucrose. The hydrolysis of the sucrose must be assumed to be a consequence of the decomposition of the ammonium chloride into ammonia and hydrogen chloride.

T. H. P.

Hydrolysis of Raffinose by means of Citric Acid. J. PIERAERTS (*Chem. Centr.*, 1906, ii, 24—25; from *Bull. Assoc. chim. Sucr. Dist.*, 23, 1143—1146).—Raffinose is completely resolved into *d*-fructose (lævulose) and melibiose by citric acid, the hydrolytic action of the acid being proportional to its concentration and to the duration of its action. The action of the citric acid may, under certain conditions, proceed further than this first stage, but the lævulose is not attacked until long after the first stage in the hydrolysis of raffinose is reached.

T. H. P.

Mechanism of Additive Reactions. VII. Reactivity of Unsaturated Nitrogen. DANIEL VORLÄNDER (*Annalen*, 1906, 345, 251—260).—The oxidation of amines is initially an additive process (compare Dunstan and Goulding, *Trans.*, 1899, 75, 1004; Wolffenstein, *Abstr.*, 1900, i, 209; Bamberger, *Abstr.*, 1902, i, 364). In its subsequent stages, the oxidation is influenced chiefly by the groups containing hydrogen adjacent to the nitrogen atom; consequently primary amines are most slowly, and tertiary amines most rapidly oxidised. Ammonium bases, which do not contain unsaturated nitrogen, are stable towards the oxidising agent. The oxidising agent used in these and the following experiments was permanganic acid in the presence of an acid. The latter on the one hand accelerates the

oxidising action of the permanganate, and on the other retards oxidation by salt-formation with the amine. In neutral or alkaline solution most amines are instantly oxidised by permanganate. The oxidation is also influenced by temperature, concentration, the presence of easily oxidisable substances which act as catalysts, and even by the products of oxidation.

Acyl derivatives are comparatively stable towards alkaline permanganate, but in acid solution are more easily oxidised than the amines, owing to the absence of salt-formation.

These results are illustrated in the paper by tables and curves.

C. S.

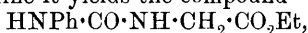
Oxidation of Ammonia Derivatives by Permanganic Acid.

DANIEL VORLÄNDER, GEORG BLAU, and THEODOR WALLIS (*Annalen*, 1906, 345, 261—276).—The paper gives a detailed account of the results mentioned in the preceding abstract, and is not suitable for abstraction.

The velocity of oxidation of an amine by acidified permanganate under carefully stated conditions is a new constant by which such substances can be identified.

C. S.

Combination of Amino-acids derived from Proteids. ALBERT MOREL (*Compt. rend.*, 1906, 143, 119—121).—When the hydrochloride of ethyl glycine is treated with a large excess of carbonyl chloride in boiling toluene, *ethyl glycine isocyanate*, $\text{CO}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, is formed. It is a colourless liquid which boils at 115—120° under 15 mm. pressure. With aniline it yields the compound



which melts at 113—114°. When boiled with water, the *isocyanate* decomposes, carbon dioxide, ethyl alcohol, and carbamidediacetic acid, $\text{CO}(\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, being formed. This acid forms well-developed crystals which melt at 166—168°.

The *isocyanate* reacts with an alkaline solution of leucine, forming the carbamide derivative,



which is insoluble in acids and melts and decomposes at 183°.

In a similar manner, with a solution of tyrosine, the *compound* $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ is formed; it crystallises from alcohol in delicate needles and melts and decomposes at 214°. These compounds do not appear to be hydrolysed under the influence of pepsin and pancreatic juice.

H. M. D.

Synthesis of Cyanogen and of Hydrogen Cyanide from their Elements. THEODOR WALLIS (*Annalen*, 1906, 345, 353—362).—Contrary to statements in the literature, cyanogen is not produced when electric sparks are passed, or the arc is established, between carbon poles in an atmosphere of nitrogen. In the presence of moisture or of hydrogen, hydrogen cyanide is formed.

In order to detect cyanogen in the presence of hydrogen cyanide, the mixture is passed into an acidified solution of a silver salt, the silver cyanide removed, the silver in the solution precipitated by yellow ammonium sulphide, a few drops of alkali are added, and after filtration

and evaporation the test for a thiocyanate is applied. The estimation of cyanogen and hydrogen cyanide is effected by passing the mixture into a solution of potassium hydroxide; the hydrogen cyanide and one-half of the cyanogen is estimated as silver cyanide; the other half, now present as potassium cyanate, is determined by boiling the cyanate with dilute sulphuric acid and titrating the ammonia produced. An alternative method is to pass the mixture into a solution of ammonium hydroxide or carbonate. After titration with a silver solution, the ammonium cyanate is converted into carbamide, and isolated and weighed as such.

Cyanogen prepared in the usual way always contains hydrogen cyanide, which can be removed by passing the gas over cotton-wool moistened with a silver solution. C. S.

Action of the Electric Discharge on Cyanogen. H. GAUDECHON (*Compt. rend.*, 1906, 143, 117—119).—When cyanogen is subjected to the action of the electric discharge, nitrogen is liberated and a solid, brown substance is formed. The composition of the deposit varies with the pressure of the gas, the capacity of the apparatus, and the potential of the discharge. It is partially, sometimes completely, soluble in water and ethyl alcohol, and always dissolves readily in dilute alkali solutions, and therefore does not contain free carbon. When heated carefully to dark redness, the solid substance gives off nitrogen, and the residue is found to be insoluble even in strong alkali solutions. The author points out that the products of the action of the discharge are thus conclusively proved to be condensation products containing excess of carbon, and do not result from the simple polymerisation of cyanogen. H. M. D.

Carbonyl Bromide. A. VON BARTAL (*Annalen*, 1906, 345, 334—353).—Emmerling and Lengyel's (Abstr., 1880, 627) or Besson's (Abstr., 1895, i, 317) methods are unsuitable for the preparation of pure carbonyl bromide. The boron tribromide required in the latter method is conveniently obtained in 60—70 per cent. yield by passing bromine vapour over powdered boron containing 10 per cent. of magnesium at a dull red heat.

Carbonyl bromide is obtained in small quantities directly from carbon monoxide and bromine vapour in the presence of aluminium bromide, or by the silent electric discharge. It is prepared in 50—60 per cent. yield by allowing sulphuric acid of sp. gr. 1·84 to drop slowly into carbon tetrabromide at 160—170°. The red distillate is shaken with mercury, distilled, shaken again with powdered antimony, and once again distilled. Pure carbonyl bromide is a heavy, mobile, colourless liquid which fumes in air, and smells somewhat like phosgene. It boils and decomposes slightly at 64—65°, has a sp. gr. 2·45 at 15°, and is decomposed by light or heat. With dimethylaniline and zinc bromide or aluminium bromide it forms dyes of the crystal-violet group, particularly hexamethyl-*p*-rosaniline hydrobromide; in the absence of the contact substance, *p*-bromodimethylaniline is produced. It is more stable towards water than carbonyl chloride. C. S.

Preparation of Cyanamides. RALPH H. MCKEE (*Amer. Chem. J.*, 1906, **36**, 208—213).—Dipropylcyanamide is obtained in a 93 per cent. yield by shaking 1.1 mols. of bromine in light petroleum solution with 1 mol. of dipropylamine and 4.5 mols. of potassium cyanide in aqueous solution below 15°. When heated with sodium methoxide in methyl-alcoholic solution at 65°, it forms *as-ψ-methyl-dipropylcarbamide*, $\text{OMe}\cdot\text{C}(\text{NH})\cdot\text{NPr}_2$, which is obtained in a yield of 80 per cent.; it boils at 98° under 19 mm., or at 203° under 748 mm. pressure, has a sp. gr. 0.9103 at 22°/4°, and is more soluble in cold than in hot water.

In a similar manner, diisobutylcyanamide, boiling at 123° under 25 mm. pressure, is obtained in an 83 per cent., diisoamylcyanamide, boiling at 134° under 14 mm. pressure, in a 92 per cent., dimethylcyanamide, boiling at 98° under 104 mm. pressure, in a 50 per cent., ethylcyanamide in a 71 per cent., benzylcyanamide, melting at 43° (33°: Strakosch, this Journal, 1872, **25**, 1026), in a 90 per cent., and cyanopiperidine, $\text{C}_5\text{NH}_{10}\cdot\text{CN}$, boiling at 102° under 11 mm. pressure, in an 80 per cent. yield. isoAmylcyanamide, $\text{C}_5\text{H}_{11}\cdot\text{NH}\cdot\text{CN}$, prepared by this method, was analysed.

Diethylcyanamide is obtained in a good yield if ethyl acetate is used in place of light petroleum, and the temperature maintained about 5°. *as-ψ-Methyldiethylcarbamide*, $\text{OMe}\cdot\text{C}(\text{NH})\cdot\text{NEt}_2$, boils at 171—172° under 745 mm. pressure, distils with water, benzene, or ether vapour, is a strong base, and can be titrated with hydrochloric acid. G. Y.

Constitution of Fulminic Acid. MILORAD Z. JOVITSCHITSCH (*Annalen*, 1906, **347**, 233—247).—The formulæ suggested by various investigators for fulminic acid are discussed, and it is pointed out that Nef's formula, $\text{C}\cdot\text{NOH}$, is not in accord with the fact that an unsaturated compound is formed in an extremely violent reaction by the action of nitric acid on alcohol. It is thought rather that Scholl's

formula, $\begin{array}{c} \text{CH}\cdot\text{N}\cdot\text{O} \\ | \\ \text{CH}\cdot\text{N}\cdot\text{O} \end{array}$, which represents the substance as glyoxime peroxide, is correct, and attempts have been made to synthesise the compound and thus solve the question of its constitution.

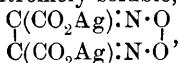
From the peroxide of ethyl diisonitrososuccinate (ethyl glyoxime peroxide-dicarboxylate), $\begin{array}{c} \text{C}(\text{CO}_2\text{Et})\cdot\text{N}\cdot\text{O} \\ | \\ \text{C}(\text{CO}_2\text{Et})\cdot\text{N}\cdot\text{O} \end{array}$, the silver salt of the dioxime

peroxide, $\begin{array}{c} \text{CAg}\cdot\text{N}\cdot\text{O} \\ | \\ \text{CAg}\cdot\text{N}\cdot\text{O} \end{array}$, was obtained. It resembles silver fulminate extremely closely, but differs from it in being easily soluble in nitric acid and in being less explosive.

Ethyl glyoxime-peroxide-dicarboxylate (ethyl azodioxazinedicarboxylate) is obtained in quantitative yield by preparing the nitrolic acid of ethyl acetoacetate, $\text{OHN}\cdot\text{C}(\text{NO}_2)\cdot\text{CO}_2\text{Et}$ (Abstr., 1892, 699), and simply evaporating its ethereal solution, when nitrous acid is eliminated and the peroxide formed.

The corresponding acid is obtained from the ester by dissolving it in concentrated sulphuric acid, and then pouring into water and extract-

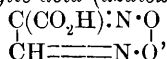
ing the oil which separates with ether; the crystalline acid melts at 96° ; its alkali salts are extremely soluble, but the *silver* salt,



is a yellowish-white powder, which is very sensitive to light and somewhat explosive.

In this hydrolysis an oil is also formed which may be an ethyl oximidoacetate, $\text{OH}\cdot\text{N}\text{:CH}\cdot\text{CO}_2\text{Et}$.

Glyoxime-peroxide-carboxylic acid (azdioxazinecarboxylic acid),



is prepared by hydrolysing the peroxide ester with sulphuric acid and dissolving the insoluble product in sodium hydroxide; it forms a thick, pale syrup, extremely soluble in water, and when treated with silver nitrate yields a yellow, extremely explosive silver salt, which is not affected by light. When the sodium salt, which is prepared by precipitating the strongly alkaline solution of the acid with alcohol, is treated with silver nitrate, the *silver* salt, $\begin{array}{c} \text{C}(\text{CO}_2\text{Ag})\text{:N}\cdot\text{O} \\ \text{CAg}=\text{N}\cdot\text{O}' \end{array}$ is formed, and exceeds all hitherto described salts in explosibility.

The *silver glyoxime peroxide (silver azdioxazine)* is prepared by treating ethyl glyoxime-peroxide-dicarboxylate with 25 per cent. sodium hydroxide under accurately defined conditions; both a *mono-* and a *di-sodium* salt can be obtained, from which both *mono-* and *di-silver* salts are prepared. The di-silver salt is a yellow powder which is not sensitive to light and is stable in the air. When treated with concentrated hydrochloric acid or heated on platinum it explodes violently. When boiled for some time with dilute hydrochloric acid, hydroxylamine is formed; but if the salt is dissolved in dilute nitric acid and hydrochloric acid then added, glyoxime peroxide can be isolated.

K. J. P. O.

Ureides. I. Action of Urethane on Pyruvic Acid and its Derivatives. LOUIS J. SIMON (*Ann. Chim. Phys.*, 1906, [viii], 8, 467—501).—A more detailed account of work already published (*Abstr.*, 1902, i, 14). G. S.

Researches in the cycloHexane Series. PAUL FREUNDLER (*Bull. Soc. chim.*, 1906, [iii], 35, 539—551).—The results recorded have, for the most part, already appeared (Freundler and Damond, *Abstr.*, 1905, i, 890, and Freundler, this vol., i, 283). The present two papers give experimental details of the methods of preparation employed.

When iodocyclohexane is heated with ethyl sodioacetoacetate in presence of alcohol, only traces of ethyl cyclohexylacetoacetate are produced, the principal product being cyclohexene. When the alcohol is replaced by xylene, scarcely any action occurs.

It was found impossible to prepare pure hexahydrobenzyl chloride by the action of hydrogen chloride or phosphorus pentachloride on the corresponding alcohol. Similar attempts to prepare hexahydrobenzyl bromide were also unsuccessful.

Acetonitrile condenses with magnesium hexahydrobenzyl iodide, yielding methylocyclohexane, a white solid containing nitrogen, and dicyclohexylethane, $C_{14}H_{26}$, a viscous, pleasant-smelling liquid, which boils at $145-150^\circ$ under 20 mm. and at $263-264^\circ$ under 762 mm. pressure.

A specimen of magnesium hexahydrobenzyl bromide, containing some hexahydrobenzyl alcohol, was condensed with ethyl acetate, and yielded a *product* boiling at $202-205^\circ$ under 45 mm. pressure, which may be the alcohol $(C_6H_{11}\cdot CH_2)_2\cdot CMe\cdot OH$. When warmed with oxalic acid at $140-150^\circ$, this was transformed into an unsaturated hydrocarbon, boiling at $143-147^\circ$ under 12-13 mm. pressure. T. A. H.

Reduction of Nitro-compounds by Tin Haloids. II. HEINRICH GOLDSCHMIDT and EINAR SUNDE (*Zeit. physikal. Chem.*, 1906, **56**, 1-42. Compare Abstr., 1904, ii, 608).—The method described previously has been further used in the study of *m*- and *o*-nitrophenols, *o*- and *p*-nitrobenzenesulphonic acids, and *o*- and *m*-nitrobenzaldehyde. The behaviour of the nitrophenols and of *m*-nitrobenzaldehyde is normal, but that of the other substances named is not so strictly in harmony with the rules deduced in the earlier paper. In the case of the two nitrobenzenesulphonic acids, it is found that an increase in the hydrochloric acid concentration is accompanied by an increase in the velocity of reduction which is greater than that required by the rule of proportionality (*loc. cit.*). Similar deviations from this rule have been observed in the case of *o*-nitrobenzaldehyde. Further, whilst the other nitro-compounds studied require 3 mols. of stannous salt for each nitro-group, it is found that *o*-nitrobenzaldehyde reacts with 2 mols. of stannous salt, and reduction beyond that stage takes place with extreme slowness, owing to the production of anthranil.

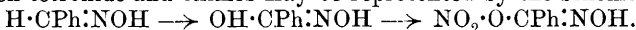
The authors' experiments show that in the reduction of nitro-compounds a part of the hydrochloric acid may be replaced by metallic chlorides without appreciably affecting the velocity of reduction. Thus the rate of reduction of *m*-nitrobenzenesulphonic acid is the same whether the solution is *N*/1 with regard to hydrochloric acid or *N*/2 with regard to hydrochloric acid and, at the same time, *N*/2 with regard to sodium or barium chloride. This observation leads to the view that the ion which is active in all these reduction processes is $SnCl_3'$ (compare *loc. cit.*).

The above-mentioned behaviour of *o*-nitrobenzaldehyde furnishes support to Haber's view of the stages in the reduction of nitro-compounds: namely, (1) $R\cdot NO_2 \rightarrow R\cdot NO$, (2) $R\cdot NO \rightarrow R\cdot NH\cdot OH$, (3) $R\cdot NH\cdot OH \rightarrow R\cdot NH_2$. The authors find that while change (2) takes place apparently in all cases with extreme rapidity, the velocity of change (3), although considerably greater than that of change (1), is measurable in many cases; the laws regulating the velocity of change (3) appear to be similar to those regulating the velocity of change (1). The substitution of $SnBr_2 + HBr$ for $SnCl_2 + HCl$, which makes the reduction change (1) eight times as rapid, makes the reduction change (3) about four times as rapid. J. C. P.

New Method of preparing the so-called Primary Dinitro-hydrocarbons. GIACOMO PONZIO (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 42—45 and 118—128).—The ordinary methods for preparing dinitro-derivatives of aliphatic hydrocarbons cannot be employed for obtaining primary dinitrohydrocarbons containing a complicated aromatic group. The latter compounds can, however, be prepared by the action of nitrogen tetroxide on ethereal solutions of the oximes (this vol., i, 593). In this way the author has obtained phenyldinitromethane, *p*-tolyldinitromethane, anisyldinitromethane, and piperonyldinitromethane.

The statement, based on the work of Scholl (Abstr., 1891, 315) and Beckmann (Abstr., 1889, 980), that the action of nitrogen tetroxide on aromatic aldoximes yields peroxides of the aldoximes, which then undergo transformation into peroxides of the dioximes, is erroneous. Only in the cases of benzaldoxime and *p*-tolualdoxime are small proportions of these peroxides formed.

Regarding the primary dinitro-hydrocarbons as nitrohydroxamic acids (Abstr., 1903, i, 786), their formation by the interaction of nitrogen tetroxide and oximes may be represented by the scheme :



p-Tolualdoxime peroxide, $\text{C}_6\text{H}_4\text{Me} \cdot \text{CH} : \text{N} \cdot \text{O} \cdot \text{O} \cdot \text{N} : \text{CH} \cdot \text{C}_6\text{H}_4\text{Me}$, prepared as described above, and also by passing nitrous acid vapours into an ethereal solution of *p*-tolualdoxime, crystallises from chloroform in shining, white plates, decomposes with a slight explosion at 121° , and dissolves in benzene.

p-Tolildioxime peroxide, $\text{C}_6\text{H}_4\text{Me} \cdot \text{C} : \text{N} \cdot \text{O} \cdot \text{O} \cdot \text{N} : \text{C} : \text{N} \cdot \text{O}$, crystallises from alcohol in shining, white needles, melts at 143° , and dissolves in ether, chloroform, or benzene, and, to a slight extent, in light petroleum.

p-Tolyldinitromethane, $\text{C}_6\text{H}_4\text{Me} \cdot \text{CH}(\text{NO}_2)_2$, crystallises from light petroleum in white plates melting at 77° , and dissolves in all the ordinary organic solvents; when heated at about 130° , it yields *p*-toluic acid. The *potassium* derivative, $\text{C}_6\text{H}_4\text{Me} \cdot \text{C}(\text{NO}_2)_2 \cdot \text{NO}_2\text{K}$, crystallises from alcohol in yellow laminae and dissolves readily in water. The *silver* derivative, $\text{C}_8\text{H}_7\text{O}_4\text{N}_2\text{Ag}$, separates from water in yellow needles and is stable under the action of light.

Anisildioxime peroxide, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C} : \text{N} \cdot \text{O} \cdot \text{O} \cdot \text{N} : \text{C} : \text{N} \cdot \text{O}$, crystallises from alcohol in shining, white needles, melting at 113° , and dissolves in light petroleum, ether, chloroform, or benzene.

Anisyldinitromethane, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{NO}_2)_2$, crystallises from light petroleum in slender needles, melting at 34° , and dissolves readily in all the ordinary organic solvents; when heated at about 130° , it gives anisic acid. The *potassium* derivative, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{NO}_2)_2 \cdot \text{NO}_2\text{K}$, crystallises from water in red laminae, which, if left in the mother liquor, rapidly change to a mass of yellow prisms. The *silver* derivative, $\text{C}_8\text{H}_7\text{O}_5\text{N}_2\text{Ag}$, separates from water in orange-yellow plates, which remain unchanged in the light.

Piperonyldinitromethane, $\text{CH}(\text{NO}_2)_2 \cdot \text{C}_6\text{H}_3 \text{ < } \overset{\text{O}}{\text{O}} \text{ > } \text{CH}_2[1:3:4]$, crystallises from light petroleum in white plates, melts at 72° , and decomposes at about 130° with evolution of red vapours. The *potassium* derivative, $\text{C}_8\text{H}_5\text{O}_6\text{N}_2\text{K}$, forms yellow prisms, soluble in water and sparingly so in alcohol.

The *silver* derivative, $\text{C}_8\text{H}_5\text{O}_6\text{N}_2\text{Ag}$, crystallises from water in red needles stable towards light. T. H. P.

Hydrolysis of Methyl Benzenesulphonate. II. ARTUR PRAETORIUS (*Monatsh.*, 1906, 27, 465—485. Compare Abstr., 1905, i, 186).—The hydrolysis of methyl benzenesulphonate by water, as also its conversion into a methyl haloid and benzenesulphonic acid by the action of a hydrohaloid acid or its salts, are side-reactions. Of these the latter is a reaction of the halogen anion, as is shown by the equivalence of the amounts of the products, and it is not accelerated by the presence of hydrogen ions.

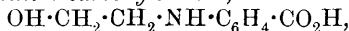
The results obtained agree with Wegscheider's formula for the hydrolysis of esters (Abstr., 1902, ii, 493). G. Y.

Nitration of Aromatic Arylsulphonamides. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 163516).—The nitro-derivatives of aromatic arylsulphonamides formerly described (Abstr., 1905, i, 639) are readily obtained by nitrating in the presence of a suitable organic solvent, such as alcohol, acetone, or benzene. When the solvent is not miscible with nitric acid, vigorous agitation is necessary.

C. H. D.

Preparation of Hydroxyethylaniline and its Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 163043).—Hydroxyethylaniline and similar compounds are obtained in good yield by heating aromatic amines with ethylene chlorohydrin and water. One mol. of the chlorohydrin and 2 mols. of the amine may be used, or the excess of the latter may be replaced by sodium acetate or carbonate. Thus aniline yields hydroxyethylaniline (Knorr, Abstr., 1889, 1218).

Hydroxyethylaniline-o-carboxylic acid,



prepared from anthranilic acid, crystallises from benzene in needles and melts at 143° .

Hydroxyethyl-o-toluidine, $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$, forms a colourless oil and boils at $285\text{—}286^\circ$.

C. H. D.

Compounds of Wool with Colourless Amines and Acids. DANIEL VORLÄNDER and A. J. PEROLD (*Annalen*, 1906, 345, 288—302).—The absorption of amines and acids by wool is similar to other chemical additive processes. In the series aniline, chloroaniline, and dichloroaniline hydrochlorides, the amount of the absorption is in the same order as the dissociation of the salt. The same holds true after the addition of hydrochloric acid, acetic acid, or acetic acid and sodium acetate, the absorption of amine being greatest in the last case.

The absorption of different acids is not in the order of their

relative strengths, probably because in a heterogeneous system adsorption, diffusion, capillarity, &c., play a part in the additive process. With acids of similar chemical character, however, the amount of absorption is in the order of their conductivities.

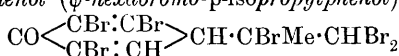
Neutral salts are not absorbed by wool, but potassium hydroxide, tetramethylammonium hydroxide, and *p*-benzeneazophenyltrimethylammonium hydroxide are very readily taken up.

There is not any essential difference between the absorption by wool or silk of coloured and colourless substances.

Extensive tables are given in the paper.

C. S.

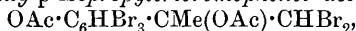
Action of Bromine and Chlorine on Phenols. Substitution Products, ψ -Bromides, and ψ -Chlorides. XVI. Hexabromo- ψ -bromide of *p*-isoPropylphenol. THEODOR ZINCKE (*Annalen*, 1906, 349, 67—82. Compare this vol., i, 172).— ψ -*p*-Tribromoiso-propyltribromophenol (ψ -hexabromo-*p*-isopropylphenol),



or $\text{OH} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CBr} \cdot \text{Me} \cdot \text{CHBr}_2$, is obtained by treating finely-powdered 3 : 5 : 3' : 5'-tetrabromo-*p*-diphenoldimethylmethane (*loc. cit.*) with a slight excess of bromine for twenty-four hours. It crystallises in colourless plates or prisms and melts at 115—116°. Cold solutions of sodium hydroxide or carbonate do not react appreciably; water acting on the substance in acetone produces pentabromoisopropylidenequinone. Cold acetic anhydride and concentrated sulphuric acid produce the *acetyl* derivative, $\text{C}_{11}\text{H}_5\text{O}_2\text{Br}_6$, which melts at 133—134° and is easily hydrolysed in cold alcoholic solution, yielding by loss of hydrogen bromide pentabromo-*p*-isopropylphenol (see below). When the ψ -hexabromide is boiled with acetic anhydride it yields tetrabromo-*p*-isopropenylphenol acetate (see below), in addition to the normal *acetyl* derivative.

p-Dibromoisopropylidenetribromoquinone (*pentabromoisopropylidenequinone*), $\text{CO} \begin{array}{c} \text{CBr} \cdot \text{CBr} \\ \text{CBr} \cdot \text{CH} \end{array} \text{C} \cdot \text{Me} \cdot \text{CHBr}_2$, is prepared by shaking an ethereal solution of the ψ -hexabromide with an equal volume of 10 per cent. sodium acetate, or as above. It separates from ether in glistening, golden-yellow needles and melts at 143—144°, and with hydrogen bromide regenerates the ψ -hexabromide.

α -Dibromo- β -acetoxy-*p*-isopropyltribromophenol acetate,



is precipitated by the addition of water to the colourless solution obtained by treating the preceding quinone with cold acetic anhydride and concentrated sulphuric acid. It separates from methyl alcohol in thick, glistening, rhombic plates, melts at 127°, and by hydrolysis yields *p*-dibromoisopropenyltribromophenol (*pentabromo-p*-isopropenylphenol), $\text{OH} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CMe} \cdot \text{CHBr}_2$, which melts at 143—144°. The last-mentioned compound is also obtained when the isomeric quinone is allowed to remain in acetone or is reduced by alkaline stannous chloride; the *acetyl* derivative, $\text{C}_{11}\text{H}_7\text{O}_2\text{Br}_5$, melts at 104—105°.

p-Bromoisopropenyltribromophenol (*tetrabromo-p*-isopropenylphenol), $\text{OH} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CMe} \cdot \text{CHBr}$, is obtained by the hydrolysis of the

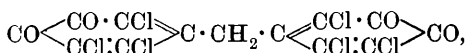
tetrabromoacetate prepared from the ψ -hexabromide, or by the reduction of the pentabromoquinone by stannous chloride in glacial acetic acid. It crystallises in colourless needles, melts at 98—99°, combines with bromine to form, in the cold the ψ -hexabromide, or at 100° the ψ -heptabromide (*loc. cit.*); its acetyl derivative separates from alcohol in rhombic leaflets, melts at 126—127°, and is identical with the acetate obtained from the ψ -hexabromide by boiling acetic anhydride. C. S.

Action of Tertiary Amines on Tetrachloro- p -cresol ψ -Bromide.
XVII. THEODOR ZINCKE and L. HUNKE (*Annalen*, 1906, 349, 83—98).—2:3:5:6-Tetrachloro-4-hydroxybenzylpyridinium bromide, $\text{OH}\cdot\text{C}_6\text{Cl}_4\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_5\text{Br}$, obtained from tetrachloro- p -cresol ψ -bromide and pyridine in ethereal solution, separates from hot glacial acetic acid in leaflets and melts and decomposes at 231°. It forms with bromine water in acetic acid glistening, yellow leaflets of a *perbromide*, with potassium dichromate a yellow, crystalline precipitate, and with potassium iodide a violet-brown, glistening *periodide*. The *platini-chloride*, $(\text{C}_{12}\text{H}_7\text{ONCl}_4)_2\cdot\text{H}_2\text{PtCl}_6$, forms yellow crystals.

The betaine derivative of 2:3:5:6-tetrachloro-4-hydroxybenzyltrimethylammonium hydroxide, $\text{C}_6\text{Cl}_4\left<\begin{smallmatrix}\text{O} \\ \text{CH}_2\end{smallmatrix}\right>\text{NMe}_3$, results when tetrachloro- p -cresol ψ -bromide in ether is treated with the calculated quantity of 30 per cent. aqueous trimethylamine. It forms a white, crystalline powder, melts and decomposes at 186°, is stable towards aqueous alkali hydroxides, but is converted by hot alcoholic solutions into tetrachloro- p -hydroxybenzyl ethyl ether (*Abstr.*, 1902, i, 282).

2:3:5:6-Tetrachloro-4-hydroxy-4'-diethylaminodiphenylmethane hydrobromide, $\text{OH}\cdot\text{C}_6\text{Cl}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{Et}_2\cdot\text{HBr}$, is obtained when the ψ -bromide is treated with a small excess of diethylaniline in ether, and forms white needles which melt and turn red at 257—258°. The free base, $\text{C}_{17}\text{H}_{17}\text{ONCl}_4$, melts at 135° and forms the corresponding salts with hydrogen chloride or bromide in glacial acetic acid. The base is stable towards hot hydrochloric acid, and is decomposed by hot dilute alkalis, diethylaniline and tarry products being formed. The *acetyl* compound forms colourless needles and melts at 120°.

Octachloro- p -diphenolmethane, $\text{OH}\cdot\text{C}_6\text{Cl}_4\cdot\text{CH}_2\cdot\text{C}_6\text{Cl}_4\cdot\text{OH}$, is obtained by the action of 5 per cent. sodium hydroxide on tetrachloro- p -cresol ψ -bromide, of water at 130—140°, or of 5—20 per cent. sodium hydroxide on the pyridinium bromide (with 1 per cent. sodium hydroxide the chief product is tetrachloro- p -hydroxybenzyl alcohol), or of concentrated sulphuric acid on tetrachloromethylenequinone, tetrachlorotoluquinol, or the isomeric tetrachloro- p -hydroxybenzyl alcohol (compare *Abstr.*, 1902, i, 282; 1903, i, 760, in which the product is regarded as a derivative of dihydroxystilbene). Octachloro- p -diphenolmethane forms colourless needles and melts at 279°; and the *acetyl* derivative, $\text{C}_{17}\text{H}_8\text{O}_4\text{Cl}_8$, at 257—258°. Nitric acid of sp. gr. 1.4 in glacial acetic acid solution converts the diphenolmethane into tetrachloro- p -quinone, whereas with acid of sp. gr. 1.5 at a gentle heat the chief product is an *o*-quinone,

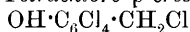


which separates from benzene in dark red crystals and dissolves in alkalis with a greenish-blue colour changing to brown (compare Abstr., 1899, i, 616).

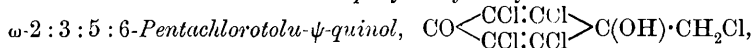
Bromine at 150° reacts with the diphenolmethane to form a mixture of substances which melts at 261° and behaves like a ψ -bromide.

C. S.

Tetrachloro-*p*-cresol- ψ -chloride. XVIII. THEODOR ZINCKE and KARL BÖTTCHER (*Annalen*, 1906, **349**, 99—106. Compare Abstr., 1902, i, 282; this vol., i, 166).—*Tetrachloro-*p*-cresol- ψ -chloride*,

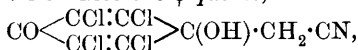


or $\text{CO} \begin{array}{c} \diagup \text{CCl} \cdot \text{CCl} \\ \diagdown \text{CCl} \cdot \text{CCl} \end{array} \text{CH} \cdot \text{CH}_2\text{Cl}$, results when tetrachloro-*p*-hydroxybenzyl alcohol is heated at 100° with an excess of hydrogen chloride in glacial acetic acid, or by chlorinating tetrachloro-*p*-cresol at 150—180°. It crystallises in long needles, melts at 145—146°, and behaves like the corresponding ψ -bromide (*loc. cit.* and preceding abstract). The *acetyl* derivative, $\text{OAc} \cdot \text{C}_6\text{Cl}_4 \cdot \text{CH}_2\text{Cl}$, melts at 118—119°, and by boiling with acetic anhydride and sodium acetate yields the diacetate of tetrachloro-*p*-hydroxybenzyl alcohol.



obtained from the ψ -chloride by the action of nitric acid of sp. gr. 1.4, forms colourless needles, melts at 137—138°, is soluble in alkali hydroxides, and by warming with sodium carbonate yields the oxide described previously (Abstr., 1902, i, 283). The *acetyl* compound, $\text{C}_9\text{H}_5\text{O}_3\text{Cl}_5$, forms colourless needles and melts at 128°.

*Tetrachloro-*p*-hydroxybenzyl cyanide*, $\text{OH} \cdot \text{C}_6\text{Cl}_4 \cdot \text{CH}_2 \cdot \text{CN}$, obtained from the ψ -chloride and potassium cyanide in aqueous acetone, separates from dilute acetic acid in leaflets or needles, melts at 208—210°, yields an *acetyl* compound melting at 140—142°, and is hydrolysed by dilute sulphuric acid (3:2) at 170—180°, yielding *tetrachloro-*p*-hydroxyphenylacetic acid*, $\text{OH} \cdot \text{C}_6\text{Cl}_4 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, which melts and decomposes at 240—242°. The cyanide is converted by nitric acid of sp. gr. 1.51 into the ψ -quinol,



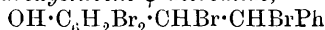
which crystallises in needles, melts and decomposes at 200—202°, and yields an *acetyl* derivative which melts and decomposes at 168°.

C. S.

Bromine Derivatives of *p*-Hydroxystilbene. XIX. THEODOR ZINCKE and W. GEIBEL (*Annalen*, 1906, **349**, 107—123).—*p*-Hydroxy- α -phenylcinnamic acid, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CPh} \cdot \text{CO}_2\text{H}$, is obtained from *p*-hydroxybenzaldehyde, sodium phenylacetate, and acetic anhydride, the resulting *acetyl* compound being hydrolysed. The acid forms small, white needles, melts at 223° with loss of carbon dioxide, and gives an *acetyl* derivative, $\text{C}_{17}\text{H}_{14}\text{O}_4$, which melts at 174°; the *methyl* ester melts at 168—169°, and its *acetyl* derivative, $\text{C}_{18}\text{H}_{16}\text{O}_4$, at 108°.

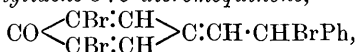
p-Hydroxystilbene, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CHPh}$, results when the preceding acid is heated rapidly to its melting point; unchanged acid is removed by sodium carbonate, and the residue, after treatment with dilute acid, is crystallised from benzene or glacial acetic acid. It separates in white leaflets, melts at 189° , and forms sparingly soluble *sodium* and *potassium* salts; the *acetyl* compound, $\text{C}_{16}\text{H}_{14}\text{O}_2$, melts at 152° .

3:5-Dibromo-4-hydroxystilbene ψ -dibromide,



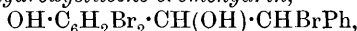
or $\text{CO}\left\langle\begin{smallmatrix}\text{CBr}:\text{CH} \\ \text{CBr}:\text{CH}\end{smallmatrix}\right\rangle\text{CH}\cdot\text{CHBr}\cdot\text{CHBrPh}$, obtained from bromine and *p*-hydroxystilbene in glacial acetic acid, crystallises in white needles, darkens at 192° , and melts and decomposes at 201° . With methyl or ethyl alcohol it yields an oily product, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}(\text{OR})\cdot\text{CHBrPh}$ (where $\text{R} = \text{Me}$ or Et). The *acetyl* derivative, $\text{C}_{16}\text{H}_{12}\text{O}_2\text{Br}_4$, obtained with acetic anhydride and concentrated sulphuric acid, forms glistening leaflets and melts at 182° .

1-Bromophenylethylidene-3:5-dibromoquinone,



formed spontaneously from the ψ -bromide in aqueous acetone, or in ethereal solution by the action of 10 per cent. aqueous sodium acetate, is an amorphous, yellow powder, which sinters at 140° and melts and decomposes at 190° ; with hydrogen bromide in glacial acetic acid the ψ -bromide is regenerated.

3:5-Dibromo-4-hydroxystilbene bromohydrin,



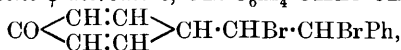
results by the slow addition of water to the ψ -bromide in acetone; it crystallises in white needles, melts at 170° , and with acetic anhydride and sulphuric acid yields the *diacetate* described subsequently.

The *acetyl* compound, $\text{CO}\left\langle\begin{smallmatrix}\text{CBr}:\text{CH} \\ \text{CBr}:\text{CH}\end{smallmatrix}\right\rangle\text{CH}\cdot\text{CH}(\text{OAc})\cdot\text{CHBrPh}$, obtained by shaking the ψ -bromide with sodium acetate and glacial acetic acid, forms a white powder, melts at 135° , yields the preceding compound on hydrolysis, and by treatment with sodium acetate and acetic anhydride forms the *diacetate*, $\text{OAc}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}(\text{OAc})\cdot\text{CHBrPh}$, which melts at $142\text{--}143^\circ$.

3:5-Dibromo-4-hydroxystilbene, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}:\text{CHPh}$, obtained from the ψ -bromide in acetone with excess of stannous chloride, crystallises in needles, melts at 150° , forms sparingly soluble salts with alkalis, yields an *acetyl* compound which melts at $130\text{--}131^\circ$, and regenerates the ψ -bromide by treatment with bromine in glacial acetic acid.

The *pyridinium bromide*, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}(\text{C}_5\text{NH}_5\text{Br})\cdot\text{CHBrPh}$, formed from the ψ -bromide and pyridine in ether, melts at $145\text{--}165^\circ$. It dissolves easily in alcohol, acetone, or glacial acetic acid, but quickly separates in the form of a white, sparingly soluble, crystalline powder, which melts and decomposes at 194° . Alkalis decompose it, yielding pyridine and an amorphous, red substance.

p-Hydroxystilbene ψ -dibromide, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHBr}\cdot\text{CHBrPh}$ or



is prepared by the action, in the dark, of the requisite quantity of bromine in ether on *p*-hydroxystilbene in ether at -15° ; it is an unstable, white powder which turns brown at 155° , melts and decomposes at 161° , and does not readily yield pure derivatives. The *acetate*, obtained by acetic anhydride and sulphuric acid, crystallises well in needles and melts and decomposes at 190 – 192° , decomposition beginning at 180° . The *quinone*, $\text{CO} \begin{smallmatrix} \text{CH:CH} \\ \text{CH:CH} \end{smallmatrix} \text{C:CH} \cdot \text{CHBrPh}$, obtained in a similar manner to the preceding quinone, is an amorphous, yellow powder, becoming white in air; it is readily soluble in the usual solvents, but cannot be crystallised. By reduction with stannous chloride in acetone it yields *p*-hydroxystilbene. The *pyridinium bromide*, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{C}_5\text{NH}_5\text{Br}) \cdot \text{CHBrPh}$, is easily soluble in alcohol, ether, or glacial acetic acid, but separates from the last solvent in a sparingly soluble modification which crystallises from hot alcohol in white needles and melts and decomposes at 175° . C. S.

4-Acetylamino-2-aminophenol-6-carboxylic Acid. LEOPOLD CASSELLA & Co. (D.R.-P. 163186).—*p*-Aminosalicylic acid is acetylated, nitrated in sulphuric acid solution, and reduced with iron and acetic acid. The *4-acetylamino-2-aminophenol-6-carboxylic acid* thus obtained crystallises from water in sparingly soluble needles, melts at 220° , and forms a sparingly soluble, yellow *diazonium* compound. C. H. D.

4-Acetylamino-2-aminophenol-6-sulphonic Acid. LEOPOLD CASSELLA & Co. (D.R.-P. 163185).—When *p*-acetylaminophenol is dissolved in sulphuric acid at 95° , an *o*-sulphonic acid is formed quantitatively. Nitric and sulphuric acids at 0° convert it into *2-nitro-4-acetylaminophenol-6-sulphonic acid*, which on reduction yields the *aminosulphonic acid*, separating from water in sparingly soluble, colourless needles and forming readily soluble salts. C. H. D.

Condensation with Anthranol. R. PADOVA (*Compt. rend.*, 1906, 143, 121–123).—Anthranol sometimes behaves as if it had the constitution of anthrone, $\text{H}_2\text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CO}$. Experiments have now been made to obtain anthrone derivatives by condensation from anthranol. When heated with benzoyl chloride in pyridine solution, anthranol yields anthraquinone and *benzoylanthranol*, which forms white needles melting at 163 – 165° .

Attempts to condense anthranol with aniline, dimethylaniline, and benzophenone gave no result, but when heated with chlorobenzophenone in xylene solution, hydrogen chloride is evolved, and on cooling crystals separate out, which have been separated by treatment with acetone. The insoluble part consists of dianthranol. From the solution, crystals are obtained which consist of yellow needles melting at 195 – 197° to a ruby-red liquid. This substance is soluble in benzene, xylene, chloroform, acetic acid, pyridine, amyl alcohol, or acetone, slightly so in methyl or ethyl alcohol, and insoluble in light petroleum. All these solutions have a colour ranging from yellow to red. It dissolves in strong sulphuric acid, forming an

emerald-green solution from which water precipitates the substance unchanged. The substance has the composition $C_{27}H_{18}O$, and is supposed to be diphenylmethylenanthraquinone, $CPh_2:C<\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}>CO$.

The molecular weight, determined by the boiling-point method, is normal in ethylene bromide, but the substance is polymerised in benzene and acetone. With benzene it yields a compound,



The Fatty Esters of Cholesterol and Phytosterol, and the Anisotropic Liquid Phases of Cholesterol Derivatives. FRANS M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 78—88).—Cholesterol and phytosterol can be easily distinguished crystallographically if the solidification of the fused material is watched on a microscopic slide. The discrete crystals as they separate from a mixture of alcohol and ether are not, on the other hand, easy to distinguish.

A number of esters of cholesterol and phytosterol with the fatty acids were prepared, preferably by boiling the alcohol with the acid anhydride, and their melting points examined. Most of the cholesterol esters examined possessed two liquid phases, namely, an anisotropic and an isotropic liquid phase; with one exception, on the other hand, the phytosterol esters have only one liquid phase. The transition points of the various cholesterol esters have been determined, and a tabular list is given in the paper. The following esters were examined: cholesterol formate, acetate, propionate, butyrate, isobutyrate, valerate, isovalerate, hexoate, octoate, decoate, benzoate, phthalate, and stearate. The formation of the anisotropic liquid was frequently accompanied by a brilliant display of colours; in some cases, namely, the formate, the octoate, and the isovalerate, the anisotropic liquid phase appeared to be labile relatively to the isotropic phase, and could only be obtained by cooling the latter suddenly. Of the phytosterol esters, on the other hand, only the valerate is anomalous, two solid phases appearing to exist, which melt respectively at 67.1° and 30° ; an anisotropic liquid phase appears also to exist.

The melting points of mixtures of cholesterol and phytosterol, and of cholesterol and phytosterol acetates, have been reinvestigated: in both cases the melting point of the substance with the lower melting point, namely, the phytosterol or the cholesterol acetate, is raised by the other constituent of the mixture.

K. J. P. O.

1:3-Dialkyl Ethers of Pyrogallol. BASLER CHEMISCHE FABRIK (D.R.-P. 162658).—The trialkyl ethers of pyrogallol or of gallic esters are decomposed when heated with hydroxides of the alkalis or alkaline earths and water under pressure, yielding 1:3-dialkyl ethers of pyrogallol. Thus, the trialkyl gallates decompose according to the equation $C_6H_2(OR)_3 \cdot CO_2R + 3NaOH = C_6H_2(OR)_2 \cdot ONa + 2R \cdot OH + Na_2CO_3$.

Pyrogallol 1:3-dimethyl ether melts at $55-56^\circ$ and boils at 258° . The *sodium* derivative forms large leaflets. *Pyrogallol 1:3-diethyl ether* crystallises from alcohol in long, colourless needles, melts at $79-80^\circ$, and boils at $263-265^\circ$.

C. H. D.

Methylenecatechol and Certain of its Derivatives. EFISIO MAMELI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 101—108).—[With ENRICO BOL.]—Catechol methylene ether, obtained in small yield by Moureu (Abstr., 1897, i, 336) by the interaction of the sodium derivative of catechol and methylene iodide, can be prepared in larger quantity by reducing an alkaline solution of the diazo-chloride of *p*-aminocatechol methylene ether (this vol., i, 93) by means of stannous chloride. When treated with nitric acid of sp. gr. 1.40, catechol methylene ether yields *p*-nitrocatechol methylene ether (compare Jobst and Hesse, Abstr., 1878, 733; 1880, 325), whilst with acid of sp. gr. 1.44—1.52, dinitrocatechol methylene ether (Jobst and Hesse, *loc. cit.*) is obtained.

p-Chlorocatechol methylene ether, $\text{CH}_2 \begin{smallmatrix} \diagup \text{O} \cdot \text{C} \cdot \text{CH} \cdot \text{CH} \\ \diagdown \text{O} \cdot \text{C} \cdot \text{CH} \cdot \text{CH} \cdot \text{Cl} \end{smallmatrix}$, prepared by the action of cuprous chloride on the diazo-chloride of *p*-aminocatechol methylene ether, is obtained as a colourless oil boiling at 185—187°. It reacts violently with concentrated nitric acid, giving a chloronitro-derivative melting at 128°.

p-Bromocatechol methylene ether, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\text{Br}$, is an oil which has a persistent, pungent odour, boils at 226—228°, dissolves readily in benzene, ether, or light petroleum, and to a less extent in alcohol, reacts energetically with concentrated nitric acid, and gives with concentrated sulphuric acid a carmine-red coloration which rapidly darkens.

p-Iodocatechol methylene ether, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\text{I}$, is obtained as a colourless oil, which boils at 156—157° under 30 mm. pressure and at 257—258° under the ordinary pressure. T. H. P.

Derivatives of Dicyanoquinol. JOHANNES THIELE and FRITZ GÜNTHER (*Annalen*, 1906, 349, 45—66. Compare Abstr., 1900, i, 299).—When an alcoholic solution of chloroquinone and concentrated sulphuric acid is treated with a strong solution of potassium cyanide at the ordinary temperature, a good yield of dicyanoquinol is obtained. The *diacetate*, $\text{C}_{12}\text{H}_8\text{O}_4\text{N}_2$, forms white leaflets and melts at 165—166°; the *methyl ether*, $\text{C}_9\text{H}_6\text{O}_2\text{N}_2\cdot\text{H}_2\text{O}$, separates from dilute alcohol in white needles and melts and decomposes at 225°, whilst its *acetate*, $\text{C}_{11}\text{H}_8\text{O}_3\text{N}_2$, melts at 136—137°. The dimethyl ether, $\text{C}_{10}\text{H}_8\text{O}_2\text{N}_2$, obtained in a sealed tube at 100° from sodium carbonate, methyl iodide, dicyanoquinol, and a little water, melts at 275°, and forms blue, fluorescent solutions in benzene or glacial acetic acid (compare Kauffmann, this vol., i, 287).

Dicyano-p-benzoquinone, $\text{C}_6\text{H}_2\text{O}_2(\text{CN})_2$, is obtained by exposing a thin layer of dicyanoquinol in a desiccator to the vapour of concentrated nitric acid under slightly reduced pressure. After purification from chloroform solution, it forms orange-red prisms and melts at 175—180°. Boiling water causes an evolution of hydrogen cyanide and the formation of dicyanoquinol and viscous by-products.

2:3-Dicyano-6-hydroxyquinol triacetate, $\text{C}_{14}\text{H}_{10}\text{O}_6\text{N}_2$, is obtained by the prolonged action of concentrated sulphuric acid and acetic anhydride on dicyanoquinone. It separates from alcohol in white needles, melts at 160°, and is easily hydrolysed by dilute sulphuric acid to 2:3-dicyano-6-hydroxyquinol, $\text{C}_8\text{H}_4\text{O}_3\text{N}_2$, which decomposes at 250°, gives

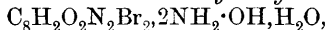
a dark green coloration with ferric chloride, and dissolves in alkalis without fluorescence. *Chlorohydroxyquinol triacetate*, $C_6H_2Cl(OAc)_3$, prepared in a similar manner from chlorobenzoquinone, forms white needles and melts at 96—97°.

Chlorodicyanoquinol, $C_8H_3O_2N_2Cl$, prepared by passing hydrogen chloride into a solution or suspension of dicyanobenzoquinone in chloroform at 0°, forms white needles, melts and decomposes at 190°, develops a violet-red coloration with ferric chloride, and dissolves in sodium carbonate solution with a yellow fluorescence; the *diacetate* melts at 122—123°.

Chlorodicyanobenzoquinone, $C_8HO_2N_2Cl$, is obtained by oxidising the preceding quinol with the vapour of nitric acid in a desiccator. It separates from chloroform in yellow needles, melts at 154—155° to a dark red liquid, is decomposed by alkalis, and reduced by sulphurous acid. Hydrogen chloride converts it into *dichlorodicyanoquinol*, $C_8H_2O_2N_2Cl_2$, which decomposes at 265° and forms a *diacetate* melting at 181—182°.

Dichlorodicyanobenzoquinone, $C_8O_2N_2Cl_2$, forms golden leaflets, decomposes at 203°, liberates iodine from hydrogen iodide, and is reduced by sulphurous acid. Water decomposes it, producing a red coloration and evolving hydrogen cyanide.

Dibromodicyanoquinol, $C_8H_2O_2N_2Br_2$, obtained by heating dicyanoquinol in glacial acetic acid with bromine (2 mols.) and potassium acetate (2 mols.), forms yellow leaflets, gives a rose-red coloration with ferric chloride, decomposes at 250°, and cannot be hydrolysed to the corresponding phthalic acid. The *hydroxylamine* salt,



forms yellow needles, decomposes when heated, and is resolved into its components by boiling water. The *diacetate*, $C_{12}H_6O_4N_2Br_2$, melts at 199°.

By treatment with acetic anhydride and a few drops of concentrated sulphuric acid, Nef's benzoquinone dibromide (Abstr., 1890, 1272) is slowly changed into 2:5-dibromoquinol diacetate.

Dibromodicyanobenzoquinone, $C_8O_2N_2Br_2$, obtained by oxidising the corresponding quinol with the vapour of nitric acid, crystallises from chloroform in purple-red leaflets, decomposes at 210—217°, and liberates hydrogen cyanide on treatment with water.

The hydrolysis of dicyanoquinol by boiling potassium hydroxide solution gives *p*-dihydroxyphthalic acid, $C_8H_6O_6$, in good yield, which separates from water in greenish-yellow needles containing $\frac{1}{2}H_2O$ and melts at 213° with loss of water. The aqueous solution develops a deep violet coloration with ferric chloride; in alkaline solution a yellow fluorescence is observed. Bromine converts the acid into bromoanil, whilst heating with ammonium carbonate forms a *p*-dihydroxyphthalimide. The *anhydride*, $C_8H_4O_5$, obtained at 220—230°, separates from benzene in greenish-yellow nodules, which by exposure to air take up $1\frac{1}{2}H_2O$ and become sulphur-yellow. The *diacetate* of the anhydride, $C_{12}H_8O_7$, separates from benzene and light petroleum in white crystals and melts at 158°.

p-*Diacetoxyterephthalic acid*, $C_{12}H_{10}O_8$, forms white nodules and is stable at 260°. The *diacetate* of the ethyl ester melts at 156·5°.

p-Diacetoxyphtthalimide, $C_{12}H_9O_6N$, separates from alcohol in white needles, becomes yellow at 150° , and melts at 200° .

Dichloro-*p*-dihydroxyphtthalimide, $C_8H_3O_4NCl_2$, obtained by heating dichlorodicyanoquinol with sulphuric acid and a trace of water, forms greenish-yellow crystals which change colour at 150° but do not melt at 270° .

Dibromo-*p*-dihydroxyphtthalimide, $C_8H_3O_4NBr_2$, separates from alcohol as a yellow powder, melts and decomposes at 250° , gives a blue coloration with ferric chloride, and a yellow fluorescence in aqueous-alcoholic solution; the diacetate melts at 263° .

p-Dimethoxyphtthalimide, obtained by hydrolysing dicyanoquinol dimethyl ether with concentrated sulphuric acid and a trace of water, forms yellow needles and decomposes at 200° .

p-Dimethoxyphtthalic anhydride, $C_{10}H_8O_5$, obtained by boiling the preceding compound with alcoholic hydrogen chloride, forms greenish-yellow crystals, melts at 259° , and gives a blue fluorescence in alcoholic acetic acid.

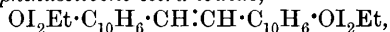
Benzoquinonedicarboxylimide, $C_6H_2O_2\langle\begin{smallmatrix} CO \\ CO \end{smallmatrix}\rangle NH$, obtained by oxidising *p*-dihydroxyphtthalimide with the vapour of nitric acid, forms brick-red leaflets, decomposes at 220° , and is readily reduced by sulphurous acid. The anhydride, $C_8H_2O_5$, prepared in similar manner from *p*-dihydroxyphtthalic anhydride, forms dark red leaflets. C. S.

Addition of Halogens and of Hydrogen Perhaloids to Oxygen Compounds. ARTHUR HANTZSCH and OSKAR DENSTORFF (*Annalen*, 1906, 349, 1—44).—The yellow modification of α -diethoxydinaphthastilbene (Elbs, Abstr., 1893, i, 271) separates from a concentrated solution in a solvent of high boiling point, and the white form from a dilute solution; if the white needles are removed from the mother liquor, the remaining yellow plates change progressively into the labile modification. The chemical properties of the two modifications are identical, and they behave as physical isomerides. On the contrary, the white and yellow modifications of dibenzoylethylene (Paal, Abstr., 1902, i, 228) are geometrical isomerides, representing the *cis*- and the *trans*-forms respectively.

The additive compounds comprise two classes: (1) perhaloids, compounds of iodine or bromine with organic oxygen compounds, especially those containing an ethereal oxygen atom; (2) hydrogen perhaloids, compounds of HBr_n and HI_n with oxygen compounds, especially unsaturated ketones such as dibenzylideneacetone.

In the formation of these substances the nature of the solvent is of the utmost importance. The most suitable are associating solvents, such as benzene, carbon disulphide, and chloroform; dissociating solvents, such as alcohol, pyridine, acetone, or water, are unfavourable.

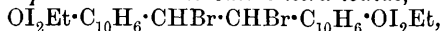
α -Diethoxydinaphthastilbene tetra-iodide,



is instantaneously obtained as a dark, voluminous precipitate when a cold solution of diethoxydinaphthastilbene in carbon disulphide, benzene, or chloroform is treated with a large excess of a concentrated

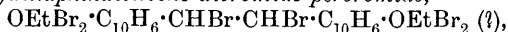
solution of iodine in the same solvent. In the dry state it is an amorphous, dark brown, compact powder, which melts and decomposes at 130—135°. By agitation with excess of carbon disulphide and of decinormal thiosulphate the iodine is removed quantitatively and the organic solvent acquires the pure yellow colour of diethoxydinaphthastilbene. In the freshly-precipitated state, the additive compound dissolves completely when rapidly heated with acetic acid, whereas a month-old preparation is only slightly soluble and decomposes by prolonged boiling.

a-Diethoxydinaphthastilbene dibromide tetra-iodide,



is obtained when the colourless dibromide is suspended in benzene and treated with a concentrated solution of iodine in the same solvent. When dry it is reddish-brown, and melts and decomposes at 146—152°.

a-Diethoxydinaphthastilbene dibromide perbromide,



is prepared by treating the dibromide, suspended in carbon disulphide at -75°, with a large excess of concentrated bromine solution. The black substance so obtained melts and decomposes at 80—95°, and loses bromine even when dried. Its composition is determined by analogy with the preceding tetraiodide. When the freshly-prepared substance is repeatedly shaken with carbon tetrachloride, glacial acetic acid, and light petroleum in succession, the added halogen is removed and the pure colourless dibromide is regenerated.

When finely-divided diethoxydinaphthastilbene is moistened with glacial acetic acid and treated with a dilute solution of bromine in the same solvent, it is instantly changed into a black substance, which, after being rapidly washed with alcohol and decomposed by alcoholic ammonia, regenerates the diethoxydinaphthastilbene. The substance is too unstable to be analysed, but is regarded as having the composition $\text{OBr}_2\text{Et}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_{10}\text{H}_6\cdot\text{OBr}_2\text{Et}$; at low temperatures it loses bromine, yielding finally almost pure normal diethoxydinaphthastilbene dibromide.

Dixanthylene tetraiodide, $\text{OI}_2\langle\text{C}_6\text{H}_4\rangle\text{C}:\text{C}\langle\text{C}_6\text{H}_4\rangle\text{OI}_2$, is a black substance which melts and decomposes at 135—140°; it is obtained as a microcrystalline powder by slow separation from the solution. The halogen is removed quantitatively by treatment with alcohol and sodium thiosulphate. In the presence of a large excess of iodine, the tetraiodide absorbs more halogen, yielding an octa- or a deca-iodide.

Dixanthylene tetrabromide is a brick-red, flocculent substance which melts and decomposes at 215—220°, and has its halogen removed quantitatively by aqueous-alcoholic sulphurous acid.

Hexane or light petroleum precipitates from a solution of iodine and dimethylpyrone in chloroform or carbon tetrachloride a yellowish-brown, viscous substance which cannot be isolated in a state suitable for analysis, but the existence of an additive compound of the two substances is indicated by the cryoscopic behaviour of their solution in ethylene dibromide, the observed depression being much smaller than the calculated value. The influence of the presence of various foreign substances has been studied, and the results, expressed graphically,

serve to confirm the existence of an additive compound of iodine and dimethylpyrone.

Bisdimethylpyrone hydrogen tribromide, $20 \left\langle \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \text{CMe} \cdot \text{CH} \end{smallmatrix} \right\rangle \text{CO} \cdot \text{HBr}_3$, is formed as an orange, flocculent precipitate on mixing solutions of dimethylpyrone and of bromine in wet ether. The substance is stable for a long time in a desiccator, separates from glacial acetic acid or chloroform in glistening, red needles, melts at $140-142^\circ$, and is insoluble in carbon disulphide, chloroform, or light petroleum. It is decolorised by alcoholic sulphurous acid or alcoholic ammonia, yielding dimethylpyrone.

Bisdibenzylideneacetone hydrogen pentaiodide, $2(\text{CHPh} \cdot \text{CH})_2 \text{CO} \cdot \text{HI}_5$, is obtained when the calculated quantity of hydrogen iodide, dissolved in benzene, is added to a dilute solution of the two components in an associating solvent. It is a voluminous, brownish-black substance, and melts and decomposes at $122-128^\circ$.

Bisdianisylideneacetone hydrogen pentaiodide,
 $2(\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH})_2 \text{CO} \cdot \text{HI}_5$,
 obtained in a similar manner, is a greyish-black, amorphous substance which melts and decomposes at $137-142^\circ$.

Bisdianisylideneacetone hydrogen tri-iodide, $2\text{C}_{19}\text{H}_{18}\text{O}_3 \cdot \text{HI}_3$, exists in two modifications. One form is obtained by repeatedly extracting the preceding pentaiodide with warm ether, ethyl acetate, or glacial acetic acid until the residue consists of small, glistening, red prisms melting at $165-167^\circ$. When a solution of this form in boiling ethyl acetate or glacial acetic acid is cooled rapidly, the second modification is obtained in the form of dense, greenish-black needles, melting and decomposing at $156-159^\circ$. The latter, which in the mother liquor undergoes partial transformation into the first, can also be obtained by bringing together dianisylideneacetone and iodine in boiling glacial acetic acid or ethyl acetate. Both forms are converted into the penta-iodide by excess of iodine dissolved in benzene; alcohol, on the contrary, removes the halogen and regenerates dianisylideneacetone.

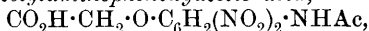
Bismonoanisylideneacetone hydrogen pentaiodide, $2\text{C}_{11}\text{H}_{12}\text{O}_2 \cdot \text{HI}_5$, separates slowly from a warm dilute solution of the ketone and iodine in carbon tetrachloride in the form of bluish-black, glistening leaflets, more quickly on addition of hydrogen iodide dissolved in benzene; it melts and decomposes at $116-122^\circ$. A pure hydrogen tri-iodide has not been obtained. At -180° the colours of all these compounds become less intense.

In conformity with the theory that iodine dissolves to a brown solution in those solvents with which it can form additive compounds, the authors find that the intensely brown solution of dimethylpyrone periodide in ethylene dibromide becomes violet by dilution; also at a suitable concentration the brown solution of the same compound in carbon tetrachloride becomes violet by warming, and brown again by cooling.

Dinaphthastilbene and its dibromide do not form additive compounds. This is one of the several arguments advanced by the authors for regarding the halogen or hydrogen perhaloid in the preceding compounds as being united to oxygen by residual affinities. C. S.

Nitration of *p*-Acetylaminophenoxyacetic Acid, of Diacetyl-*p*-aminophenol, and of *p*-Acetanisidine. FRÉDÉRIC REVERDIN and ARTHUR BUCKY (*Arch. Sci. phys. nat.*, 1906, [iv], 22, 124—145).—As with benzoyl- and dibenzoyl-*p*-aminophenol (Reverdin and Delétra, this vol., i, 165, 273), so also with *p*-acetylaminophenoxyacetic acid, nitration with a mixture of sulphuric and nitric acids yields products different from those obtained by using nitric acid alone (compare Howard, Abstr., 1898, i, 29).

2 : 5-Dinitro-4-acetylaminophenoxyacetic acid,



obtained by the action of sulphuric and nitric acids on *p*-acetylaminophenoxyacetic acid, crystallises in yellow to orange-yellow needles or plates melting at 176°, and dissolves readily in acetic acid, acetone, acetic anhydride, or solutions of the alkali hydroxides or carbonates, to a less extent in alcohol, and only sparingly in benzene or chloroform. Its barium salt (+ 2H₂O) crystallises in small, yellowish-brown prisms slightly soluble in cold water.

2 : 5-Dinitro-4-aminophenoxyacetic acid,



prepared by hydrolysing the acetyl derivative by means of concentrated sulphuric acid, crystallises from water in orange-red needles or plates, melts at 170°, and dissolves readily in alcohol, acetone, acetic acid, or solutions of the alkali hydroxides or carbonates. Its barium salt (+ 3H₂O) separates in brownish-red needles. Its ethyl ester crystallises in silky, red needles melting at 144°, and is soluble in acetic acid or benzene. When diazotised and treated with sulphuric acid and potassium iodide, the acid gives (1) an *iodo*-acid, which crystallises from light petroleum in faintly orange, yellow plates, melts at 114—115°, and dissolves in alcohol, benzene, acetic acid, chloroform, or dilute acetone; its sodium salt separates in slender, orange needles, its potassium salt in red crystals, and its barium salt in brown crystals; (2) another *iodo*-acid, crystallising from dilute acetic acid in yellow, flattened needles melting at 201—202°, and dissolving readily in acetone or alcohol and sparingly in benzene or chloroform; its barium salt forms yellowish-brown, prismatic needles.

Howard (*loc. cit.*) has assigned an erroneous structure to the acid obtained by the action of nitric acid alone on *p*-acetylaminophenoxyacetic acid, the authors' results showing that 2 : 3-dinitro-4-acetylaminophenoxyacetic acid is obtained under these conditions. The mother liquors from this acid are found to contain another acid, giving, on partial hydrolysis with concentrated sulphuric acid, 3 : 5-dinitro-4-aminophenoxyacetic acid, C₈H₇O₇N₃, which crystallises from water in long, red needles melting at 190°, and dissolves in alcohol or acetic acid, and to a slight extent in benzene; this acid is decomposed by alcohol, yielding a dinitrophenoxyacetic acid (?), which separates as a pale yellow, crystalline powder melting at 207°.

When diacetyl-*p*-aminophenol is nitrated by means of a mixture of sulphuric and nitric acids, the acetyl derivative of isopicramic acid, melting at 181°, is obtained. In this case, therefore, just as with dibenzoyl-*p*-aminophenol (Reverdin and Dresel, Abstr., 1905, i, 51), one of the acetyl groups first undergoes hydrolysis to hydroxyl. If,

however, a mixture of sulphuric and nitric acids is added to a sulphuric acid solution of diacetyl-*p*-aminophenol containing acetic anhydride, a compound, $C_7H_6O_6N_3$, is obtained, which crystallises from dilute alcohol in golden-brown needles, decomposes at 163.5° , and dissolves in water or dilute acetic acid, and to a slight extent in benzene.

The nitroacetylanisidine [$OMe : NO_2 : NHAc = 1 : 2 : 4$] of the Farbwerke vorm. Meister, Lucius, & Brünig (D.R.-P. 101778) crystallises from dilute acetic acid or aqueous alcohol in orange-yellow needles melting at $148-149^\circ$, and is soluble in water and slightly so in benzene or light petroleum. When *p*-acetylanisidine is nitrated by means of sulphuric and nitric acids it yields (1) the dinitro-*p*-acetylanisidine melting at 157° (Meldola and Stephens, Trans., 1905, 87, 1199), and (2) a new dinitro-*p*-acetylanisidine [$OMe : (NO_2)_2 : NHAc = 1 : 2 : 5 : 4$], which crystallises from dilute acetic acid in lemon-yellow crystals, melts at $175.5-176.5^\circ$, and dissolves readily in acetone, less so in alcohol, and sparingly in water, benzene, or light petroleum. Hydrolysis of the latter compound yields the corresponding dinitro-*p*-anisidine [$OMe : (NO_2)_2 : NH_2 = 1 : 2 : 5 : 4$], which crystallises from a mixture of benzene and light petroleum in red needles melting at 153° , and is soluble in alcohol or acetic acid and readily so in benzene; it does not dissolve in a solution of sodium carbonate, or hydroxide, or ammonia, but gives a violet-red coloration which changes to yellow under the influence of heat.

T. H. P.

Preparation of Indoxyl and its Homologues. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 163039).—Compounds containing the group $-NR \cdot CH_2 \cdot CO-$ ($R = \text{aryl}$), such as phenylglycine, phenylglycinephenylglycine, or their homologues, salts, esters, or amides, also phenylhydantoin and diphenylhydantoin, or their homologues, yield derivatives of indoxyl when heated with the alkali or alkaline earth metals or their alloys. The violence of the reaction is moderated by the addition of alkali hydroxides or cyanides.

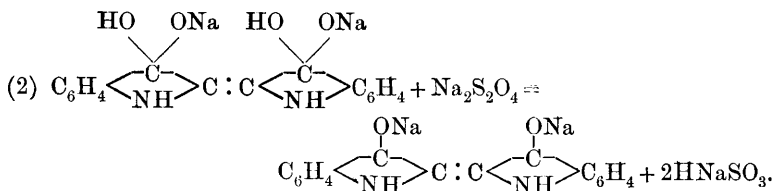
Thus, potassium phenylglycine and an alloy of lead and sodium, added to a fused mixture of potassium and sodium hydroxides, give a product which yields 40—50 per cent. of indigotin on oxidation.

C. H. D.

Addition of Alkali to Indigotin. ARTHUR BINZ (*Zeit. angew. Chem.*, 1906, 19, 1415—1418).—When powdered indigo is shaken for several days with alcoholic sodium hydroxide, a dark green powder is obtained which has the composition $C_{16}H_{10}O_2N_2 \cdot NaOH$; on exposure to the air, or on mixing with water, this substance turns blue with liberation of indigotin and sodium hydroxide; if the reaction is carried out at a temperature of 60° it is completed in a few minutes.

The corresponding compound, $C_{16}H_{10}O_2N_2 \cdot C_6H_5 \cdot ONa$, which is obtained by heating powdered indigo for some minutes to 77° with alcoholic sodium phenoxide, is a dark green solid. It is assumed accordingly that the reactions taking place in the indigo vat may be represented as follows:





If equation (2) is correct, the reaction should be facilitated by the addition of alcohol, which diminishes hydrolysis. This was shown to be the case by experiment, in which it was found that the reaction took place about thirty times more quickly in alcoholic than in aqueous solution.

P. H.

Preparation of the Three Phthalaldehydes. JOHANNES THIELE and OSKAR GÜNTHER (*Annalen*, 1906, 347, 106—111).—*o*-Phthalaldehyde is prepared by boiling ω -tetrabromo-*o*-xylene with potassium oxalate and dilute alcohol for forty hours until the whole has dissolved to a pale yellow solution, carbon monoxide and dioxide being evolved. After evaporating the solvent, the aldehyde is distilled in a current of steam and the distillate, after saturation with sodium sulphate, extracted with ethyl acetate. The pure aldehyde, crystallising in yellow needles melting at 56—56.5°, is obtained in a yield of 90 per cent.

[With LEOPOLD.]—*m*-Phthalaldehyde is prepared from ω -tetrabromo-*m*-xylene, $\text{C}_6\text{H}_4(\text{CHBr}_2)_2$, which crystallises in colourless needles melting at 107°. The tetrabromide is converted into corresponding aldehyde in a similar manner to the *o*-derivative; it is purified by conversion into the *trialdehydohydrobenzamide*, $(\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH})_3\text{N}_2$, which is a white, insoluble powder. The aldehyde crystallises in colourless needles melting at 89.5°; the dioxime melts at 180°.

K. J. P. O.

Condensation Products of *o*-Phthalaldehyde. JOHANNES THIELE and KAUFMAN G. FALK (*Annalen*, 1906, 347, 112—131).—2-Acetyl-3-hydrindone (2-acetyl-3-hydroxyindene), $\text{C}_6\text{H}_4 \text{---} \text{CH}_2 \text{---} \text{CHAc}$ or



prepared by treating phthalaldehyde and acetone with potassium hydroxide, crystallises in pale yellow needles melting at 76.5°, and is readily soluble in alkali hydroxides; it yields a red coloration with ferric chloride in alcoholic solution, which becomes violet on addition of water. When bromine is added to its alkaline solution, 2:2-dibromohydrindone is obtained. The *phenylhydrazone* of acetylhydrindone crystallises in yellow, flattened needles or leaflets melting at 169—170°, and when treated with hydrochloric acid in methyl-alcoholic solution is converted into a *pyrazole* derivative, $\text{C}_{17}\text{H}_{14}\text{N}_2$, which crystallises in colourless prisms and melts at 84°.

Benzoylhydrindone (2-benzoyl-3-hydroxyindene), $\text{C}_6\text{H}_4 \text{---} \text{CH}_2 \text{---} \text{CHBz}$ or $\text{C}_6\text{H}_4 \text{---} \text{CH}_2 \text{---} \text{C(OH)} \text{---} \text{CBz}$, is prepared in a similar manner from *o*-phthalaldehyde and acetophenone; it crystallises in yellow plates or

pale yellow needles melting at 98.5° , and gives a deep green coloration with ferric chloride; by bromine it is converted into dibromohydrindone. Phenylhydrazine converts it into a corresponding pyrazole, $C_{22}H_{16}N_2$, which crystallises in red needles melting at 174° .

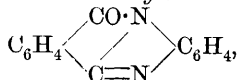
The *diphenylhydrazone* of *o*-phthalaldehyde, $C_6H_4(CH:N_2HPh)_2$, crystallises in golden-yellow needles melting at 190 – 191° . When boiled with dilute hydrochloric acid, it is converted into *1-hydroxy-2-phenyl-1:2-dihydrophthalazine*, $C_6H_4 \begin{smallmatrix} \text{CH}(\text{OH}) \cdot \text{NPh} \\ \text{CH} = \text{N} \end{smallmatrix}$, which forms colourless crystals melting at 128 – 129° ; its *methyl* ether is formed on merely dissolving the compound in methyl alcohol and forms white crystals melting at 59 – 60° ; the *ethyl* ether melts at 96 – 97° ; both ethers are reconverted into the original substance by dissolving them in acids and precipitating with an alkali.

Phenylphthalazonium chloride, $C_6H_4 \begin{smallmatrix} \text{CH} \cdot \text{NPhCl} \\ \text{CH} \cdot \text{N} \end{smallmatrix}$, is prepared by passing dry hydrogen chloride into a solution of the hydroxydihydrophthalazine or one of its ethers in benzene; it crystallises in white needles melting at 106 – 107° , and is readily soluble in water. Its *aurichloride* crystallises in yellow needles melting at 181° ; its *platini-chloride* forms orange-red crystals melting at 224 – 225° .

Phenylphthalazone, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{NPh} \\ \text{CH} \cdot \text{N} \end{smallmatrix}$, formed by oxidising the hydroxyphthalazine with alkaline permanganate, crystallises in needles melting at 106° , and is identical with the anhydride obtained by Racine (Abstr., 1887, 951) and Henriques (Abstr., 1888, 842) from phenylhydrazinephthalaldehydic acid.

o-Benzylenebenziminazole, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{N} \\ \text{C} = \text{N} \end{smallmatrix} C_6H_4$, prepared by heat-

ing *o*-phthalaldehyde and *o*-phenylenediamine hydrochloride in aqueous solution and then precipitating the base with alkali, crystallises in needles melting at 210° , and yields a *hydrochloride* crystallising in needles; the *sulphate* crystallises in sparingly soluble leaflets; the *platinichloride* forms yellow crystals. When oxidised by permanganate in acid solution, a mixture of *benzoylenebenziminazole*,



and phenylbenziminazole-*o*-carboxylic acid, $C_6H_4 \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} C \cdot C_6H_4 \cdot \text{CO}_2H$, is obtained; the former crystallises in yellow needles melting at 211 – 212° , and when boiled with alkalis or acids is rapidly hydrolysed to the latter, which melts at 273° . It is found to be identical with the "phthalyl-*o*-phenylenediamine" melting at 266° , prepared by Anderlini (Abstr., 1894, i, 375) from phthalic anhydride and *o*-phenylenediamine. The *ethyl* ester, $C_{16}H_{14}O_2N_2$, crystallising in leaflets melting at 163 – 164° , was obtained from the acid prepared by both methods. The *platini-chloride*, $C_{32}H_{30}O_4N_4 \cdot PtCl_6$, obtained from the ester, is a yellow pre-

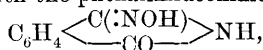
cipitate. When the acid is heated at 280—290°, or treated with acetic anhydride, it is reconverted into benzoylenebenziminazole.

o-Tolylenediamine and *o*-phthalaldehyde similarly yield *o*-benzoylene-

toliminazole, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{C} = \text{N} \end{array} \text{C}_6\text{H}_3\text{Me}$, which forms colourless crystals

melting at 192—193°; the *platinichloride* is a yellow precipitate.

The *compound* obtained by the action of hydroxylamine on *o*-phthalaldehyde is identical with the phthalimideoxime,



prepared by Müller (Abstr., 1886, 802).

K. J. P. O.

Thio-derivatives of Aromatic Aldehydes and Ketones and their Desulphurisation. WILHELM MANCHOT and CHR. ZAHN (*Annalen*, 1906, **345**, 315—334. Compare Abstr., 1905, i, 342).—*Dithiopiperonaldehyde*, $\text{C}_7\text{H}_5\text{O}_2 \cdot \text{CH}_2 \cdot \text{S} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{C}_7\text{H}_5\text{O}_2$, results after two to four weeks by the addition of finely-powdered piperonaldehyde to saturated alcoholic ammonium sulphide; it separates from alcohol and acetone in short, white prisms, melts at 69·5°, gives a carmine-red coloration with concentrated sulphuric acid, and is reduced by zinc dust and glacial acetic acid to the *mercaptan*, $\text{C}_8\text{H}_7\text{O}_2 \cdot \text{SH}$, a yellow oil which forms yellow *lead* and *copper* salts, a greenish-yellow *silver* salt, and is reconverted into the disulphide by alcoholic iodine.

Dithiopiperonaldehyde hydrosulphide, $\text{C}_{16}\text{H}_{14}\text{O}_4\text{S}_2 \cdot \text{H}_2\text{S}$, results when alcoholic ammonium sulphide containing excess of hydrogen sulphide is used, and the mixture shaken for many days; it crystallises in slender needles, melts at 113°, does not form mercury or lead salts, is reduced to the mercaptan, and readily loses sulphur by treatment with a solution of sodium ethoxide or with copper powder.

Bis-3:4-methylenedioxydibenzyl, $\text{C}_{16}\text{H}_{14}\text{O}_4$, obtained from the disulphide and copper powder at 280° or by prolonged boiling in xylene, separates from alcohol in slender needles, melts at 138°, and yields a *bromide*, $\text{C}_{16}\text{H}_{12}\text{O}_4\text{Br}_2$, which melts at 164°.

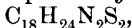
Dithiovanillin, $\text{C}_{16}\text{H}_{18}\text{O}_4\text{S}_2$, obtained in a similar manner to the preceding disulphide, melts at 129—130°, loses sulphur by treatment with concentrated sulphuric acid or sodium hydroxide, and hydrogen sulphide by treatment with zinc dust and acetic acid; the *benzoyl* derivative, $\text{C}_{30}\text{H}_{26}\text{O}_6\text{S}_2$, melts at 133—135°, and does not form mercury or lead salts. *Dithiobromovanillin*, $\text{C}_{16}\text{H}_{16}\text{O}_4\text{Br}_2\text{S}_2$, prepared from Tiemann's bromovanillin, melts at 159°.

4:4'-Dihydroxy-3:3'-dimethoxydibenzyl, $\text{C}_{16}\text{H}_{18}\text{O}_4$, obtained from copper powder and dithiovanillin by heating alone or in xylene solution, forms long, slender needles, melts at 158°, produces a mirror with ammoniacal silver solutions, and yields a *bromide*, $\text{C}_{16}\text{H}_{14}\text{O}_4\text{Br}_4$, which melts at 214°.

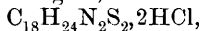
Dithioanisaldehyde, $\text{C}_{16}\text{H}_{18}\text{O}_2\text{S}_2$, prepared previously in an impure state by Baumann and Fromm (Abstr., 1891, 1050), melts at 101°, and by careful heating with copper powder, alone or in xylene solution, yields *p*-bismethoxydibenzyl, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, which separates from alcohol in large needles, develops a magnificent red

coloration with ferric chloride and concentrated sulphuric acid, and yields a *bromide*, $C_{16}H_{16}O_2Br_2$, which melts at 147° .

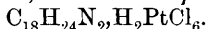
[By G. KRÄNZLEIN.]—*Dithio-p-dimethylaminobenzaldehyde*,



prepared like the preceding disulphides or by heating *p*-dimethylaminobenzaldehyde and ammonium sulphide at 100 – 120° , separates from alcohol in elongated prisms, melts at 83.5° , yields the *mercaptan* by reduction with sodium amalgam, and forms a *hydrochloride*,



which melts at 211° . *Bis-p-dimethylaminodibenzyl*, $C_{18}H_{24}N_2$, boils at 105° under 25 mm. pressure, and forms a *platinichloride*,



When *p*-dimethylaminobenzaldehyde is treated with alcoholic ammonium sulphide containing excess of hydrogen sulphide, a *hydro-sulphide*, $C_{18}H_{24}N_2S_2 \cdot H_2S$, is obtained, which melts at 162° .

Bis-3:4-methylenedioxy stilbene, $C_7H_5O_2 \cdot CH:CH \cdot C_7H_5O_2$, obtained by heating α -trithiopiperonaldehyde (Wörner, Abstr., 1896, i, 225) and copper above 200° , separates from glacial acetic acid in short prisms and melts at 206° .
C. S.

Reaction between Unsaturated Compounds and Organic Magnesium Compounds. IX. Reactions with Stereoisomerides. ELMER P. KOHLER (*Amer. Chem. J.*, 1906, **36**, 177–195. Compare this vol., i, 427; Kipping and Salway, *Trans.*, 1904, **85**, 438).—The action of magnesium ethyl bromide on benzylidenedeoxybenzoin and *isobenzylidenedeoxybenzoin*, and treatment of the product with water or hydrochloric acid cooled with ice, leads to the formation of the two forms of $\alpha\beta$ -diphenylvalerophenone, the relative amounts of the isomerides contained varying with the method of isolation. The action of benzoyl chloride on the magnesium compounds from the two isomerides results in the formation of the same $\alpha\beta$ -*triphenyl- Δ^a -pentenyl benzoate*, $CH_2EtPh \cdot CPh \cdot CPh \cdot O \cdot CPh$, which crystallises from alcohol in long needles, melts at 143° , is not changed by heating at 150° for forty hours or by exposure to sunlight in benzene iodine solution, and on hydrolysis with aqueous potassium hydroxide cooled by ice or with concentrated hydrochloric acid at 150° yields the $\alpha\beta$ -diphenylvalerophenone melting at 170° . The product obtained on hydrolysis of the benzoate with boiling alcoholic hydrogen chloride contains 10 per cent., or, with cold alcoholic hydrogen chloride, 14 per cent., of the isomeric ketone melting at 92° . The ketone melting at 92° is converted rapidly by potassium hydroxide, more slowly by hydrochloric acid, into its isomeride melting at 170° .

$\alpha\beta$ -Triphenyl- Δ^a -pentenyl acetate, $CH_2EtPh \cdot CPh \cdot CPh \cdot OAc$, formed in a similar manner to the benzoate, crystallises in slender needles, melts at 120° , and on hydrolysis behaves in the same manner as the benzoate.

If the additive compound of magnesium ethyl bromide and benzylidene- or *isobenzylidenedeoxybenzoin* is poured on to ice and ether free from alcohol, it yields an oil which is probably *$\alpha\beta$ -triphenyl- Δ^a -pentenol*, $CH_2EtPh \cdot CPh \cdot CPh \cdot OH$; this is readily soluble in cold light petroleum, reduces potassium permanganate in acetone solution, and in

a freezing mixture changes slowly into $\alpha\beta$ -diphenylvalerophenone, of which 99.62 per cent. melts at 92° and 0.38 per cent. at 170° . When a current of air is passed through the moist ethereal solution of the enol cooled by a freezing mixture, the *peroxide*, $\text{CHEtPh}\cdot\text{CPh}\langle\begin{smallmatrix} \text{O}_2 \\ \text{CPh}\cdot\text{OH} \end{smallmatrix}\rangle$,

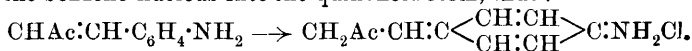
is formed in two modifications, one of which crystallises from acetone in stout needles and melts at 166° ; the other crystallises in large, transparent prisms and melts at 109° . These peroxides are not formed by the action of air or oxygen on $\alpha\beta$ -diphenylvalerophenone; they are stable, do not yield hydrogen peroxide with water, do not liberate iodine from iodides, do not oxidise indigo, when heated in quantity decompose with a flash but without detonation, forming benzoic acid and ethyldeoxybenzoin, and react with magnesium ethyl bromide forming a *product* from which the peroxides are again formed on treatment with ice.

$\alpha\beta\gamma\gamma$ -Tetraphenyl- Δ^a -propenol, $\text{CHPh}_2\cdot\text{CPh}\cdot\text{CPh}\cdot\text{OH}$, prepared by the action of magnesium phenyl bromide on benzylidenedeoxybenzoin in light petroleum solution, and treatment of the product with ice and ether free from alcohol, separates from light petroleum in colourless needles, melts at about 95 — 100° , and changes into triphenylpropionophenone when slowly heated below its melting point. The *peroxide*,

$\text{CHPh}_2\cdot\text{CPh}\langle\begin{smallmatrix} \text{O}_2 \\ \text{CPh}\cdot\text{OH} \end{smallmatrix}\rangle$, crystallises in small, lustrous prisms, melts at 127° , and when heated alone, or with hydrochloric acid in alcoholic solution, decomposes, forming benzoic acid and diphenylacetophenone (Delacre, Abstr., 1896, i, 486; Biltz, Abstr., 1899, i, 439); this forms an *additive* compound with magnesium ethyl bromide, which reacts with water, yielding the *alcohol*, $\text{CHPh}_2\cdot\text{CEtPh}\cdot\text{OH}$, crystallising in needles and melting at 91° . The *oxime* of diphenylacetophenone, $\text{CHPh}_2\cdot\text{CPh}\cdot\text{NOH}$, is obtained in small yields by the action of hydroxylamine hydrochloride on the ketone in aqueous potassium hydroxide solution. It crystallises from acetone in plates and melts at 182° .

Bromotriphenylpropionophenone, $\text{CHPh}_2\cdot\text{CBrPh}\cdot\text{COPh}$, prepared by treating the magnesium derivative of tetraphenylpropenol with bromine, crystallises in large prisms, melts at 124° , and readily loses hydrogen bromide. G. Y.

Methinammonium Compounds. HANS RUPE and A. PORAI-KOSCHITZ (*Zeit. Farb. Ind.*, 1906, 5, 317—321).—The coloured salts of *p*-aminobenzylideneacetone are thought to be produced by a transition of the benzene nucleus into the quinonoid form, thus:



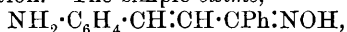
In order to test this hypothesis, it was necessary to investigate the *m*-amino-compounds. Since the acetone derivatives are difficult to prepare, the corresponding acetophenone derivatives have been studied.

m-Aminobenzylideneacetophenone, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COPh}$, prepared by reducing the corresponding nitro-derivative with stannous chloride in acetic acid solution, crystallises in pale yellowish-green, rhombic leaflets melting at 159° ; it dissolves in hydrochloric acid, forming

a completely colourless solution, from which the *hydrochloride* can be isolated as colourless needles. The *sulphate* is similar. The *acetyl* derivative, prepared from the hydrochloride and acetic anhydride in the presence of sodium acetate, crystallises in yellow, prismatic needles melting at 104°.

p-Aminobenzylideneacetophenone crystallises in golden leaflets melting at 151°; it dissolves in moderately dilute hydrochloric acid, forming a deep red solution, which becomes decolorised by addition of concentrated hydrochloric acid, flesh-coloured needles finally separating. These crystals dissolve in hot concentrated hydrochloric acid with a red coloration, which, however, disappears on cooling. If water is cautiously added to the red solution, red crystals separate. Both forms have the same composition, $C_{15}H_{13}ON \cdot HCl$. The solution of the base in acetic acid is deep red, and deposits dark red leaflets, which, on slowly heating, fade in colour, and finally melt at 151°, the melting point of the base. The *acetyl* derivative crystallises in pale green leaflets melting at 179°.

p-Aminoacetophenone and hydroxylamine yield two compounds according as sodium hydroxide or carbonate has been used to bring about the condensation. The simple *oxime*,



is formed in the presence of the hydroxide, and crystallises in leaflets melting at 139°. In presence of sodium carbonate, an *oximido-oxime*, $NH_2 \cdot C_6H_4 \cdot CH(NH \cdot OH) \cdot CH_2 \cdot CPh : NOH$, is produced, and crystallises in needles melting at 178.5—179°; the *hydrochloride* is sparingly soluble.

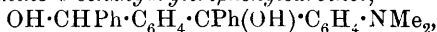
p-Dimethylaminobenzylideneacetophenone forms a bluish-grey hydrochloride when treated with a small quantity of fuming hydrochloric acid; the solution in hydrochloric acid is blue. The base dissolves in dilute hot hydrochloric acid with a deep red coloration, which disappears on cooling, the solution depositing a colourless, crystalline *hydrochloride*, $C_{17}H_{17}ON \cdot HCl$, crystallising in needles; this material again dissolves in hot acid with a red coloration. In concentrated sulphuric acid, the base forms a colourless solution, from which a small quantity of water precipitates a colourless sulphate. The solution in hot acid is red. The *phenylhydrazone* of *p*-dimethylaminobenzylideneacetophenone, $NMe_2 \cdot C_6H_4 \cdot CH : CH \cdot CPh : N \cdot NHPh$, forms very pale green needles melting at 127—128°. K. J. P. O.

Action of Magnesium Phenyl Bromide on Dialkylaminobenzoylbenzoic Esters. J. PÉRARD (*Compt. rend.*, 1906, 143, 237—239).—2-Hydroxy-1-*p*-dimethylaminophenyl-1 : 2-diphenyl-1 : 2-dihydroisobenzofuran, $\begin{array}{c} C_6H_4 \\ | \\ CPh \cdot C_6H_4 \cdot NMe_2 \\ | \\ CPh(OH) \cdot O \end{array}$, prepared by the action

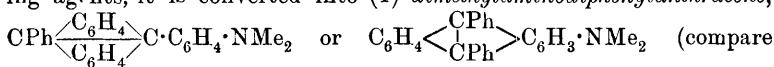
of excess of magnesium phenyl bromide on methyl dimethylaminobenzoylbenzoate (Haller and Guyot, *Abstr.*, 1904, i, 602), crystallises from a mixture of benzene and alcohol in slender, faintly yellow needles melting at 194° (uncorr.), and dissolves in the hydrocarbons, to a less extent in the alcohols, and sparingly in ether or acetone. It is soluble in acids, forming intensely red salts, which crystallise from acetone in slender needles and are dissociated by water. The *picrate*

melts and decomposes at 246° . The *methyl* and *ethyl* ethers crystallise from a mixture of benzene and alcohol in colourless prisms and melt at 158° and 169° respectively.

p-Dimethylamino-*o*-benzhydryltriphenylcarbinol,



prepared by reducing the preceding compound by means of sodium amalgam and alcohol, separates from a mixture of alcohol and ether in white crystals and melts at 145° . Under the action of dehydrating agents, it is converted into (1) *dimethylaminodiphenylanthracene*,



Guyot and Catel, *Abstr.*, 1905, i, 516), which separates from a mixture of benzene and light petroleum in microscopic, green crystals melting at 298° , and dissolves in acetic acid, carbon disulphide, or pyridine, and, to a slight extent, in alcohol; or (2) 1-*p*-dimethylamino-phenyl-1:2-diphenyl-1:2-dihydroisobenzofuran, $\begin{array}{c} \text{C}_6\text{H}_4 - \text{CPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2 \\ | \\ \text{CHPh} \cdot \text{O} \end{array}$,

which crystallises from a mixture of benzene and alcohol in white prisms melting at 110° . T. H. P.

Introduction of Dinaphthapyryl and Xanthyl Radicles into Electro-negative Molecules. ROBERT FOSSE and A. ROBYN (*Compt. rend.*, 1906, 143, 239—242).—Dinaphthapyryl and xanthyl radicles can readily be substituted for a hydrogen atom of various electro-negative organic molecules, such as β -ketonic esters, β -diketones, or ethyl malonate or cyanoacetate, by: (1) the action of heat on a molecular mixture of xanthydrol with a β -ketonic or cyanoacetic ester; (2) contact in an acetic acid medium of either xanthydrol and a β -ketone or dinaphthapyranol and an acetoacetic ester; (3) double decomposition between dinaphthapyryl bromide and the sodium derivative of a β -ketonic ester, a β -diketone, or a malonic or cyanoacetic ester.

It has not been determined whether the union of the two constituent radicles of the compounds thus obtained is by means of carbon-carbon, carbon-oxygen, or oxygen-oxygen.

The following new compounds have been prepared:

Ethyl xanthylacetoacetate, $\left[\text{O} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{CH} \right] [\text{CHAc} \cdot \text{CO}_2\text{Et}]$, forms white, nacreous crystals and melts at 87 — 89° .

Ethyl xanthylethylacetoacetate, $[\text{O}(\text{C}_6\text{H}_4)_2\text{CH}][\text{CEtAc} \cdot \text{CO}_2\text{Et}]$, prepared by the action of sodium and ethyl iodide on the preceding compound, forms plates melting at 126 — 127° .

Ethyl xanthylbenzoylacetoacetate, $[\text{O}(\text{C}_6\text{H}_4)_2\text{CH}][\text{CHBz} \cdot \text{CO}_2\text{Et}]$, forms groups of white needles melting at 80° .

Dinaphthapyrylacetylacetone, $\left[\text{O} \begin{array}{c} \text{C}_{10}\text{H}_6 \\ \diagup \quad \diagdown \\ \text{C}_{10}\text{H}_6 \end{array} \text{CH} \right] [\text{CHAc}_2]$, forms colourless crystals melting at 155 — 157° (uncorr.).

Xanthylacetylacetone, $[\text{O}(\text{C}_6\text{H}_4)_2\text{CH}][\text{CHAc}_2]$, crystallises in long, white needles melting at 141 — 142° (uncorr.).

Dinaphthapyrylbenzoylacetoacetone, $[\text{O}(\text{C}_{10}\text{H}_6)_2\text{CH}][\text{CHAcBz}]$, forms colourless crystals melting and decomposing at about 201 — 204° .

Xanthylbenzoylacetone, $[\text{O}(\text{C}_6\text{H}_4)_2\text{CH}][\text{CHAcBz}]$, forms white crystals melting at 171° (uncorr.).

Ethyl dinaphthapyrylmalonate, $[\text{O}(\text{C}_{10}\text{H}_6)_2\text{CH}][\text{CH}(\text{CO}_2\text{Et})_2]$, forms large, colourless crystals melting at $109\text{--}110^\circ$.

Ethyl dinaphthapyrylcyanoacetate, $[\text{O}(\text{C}_{10}\text{H}_6)_2\text{CH}][\text{CN}\cdot\text{CH}\cdot\text{CO}_2\text{Et}]$, melts at $158\text{--}159^\circ$ (uncorr.).

Ethyl xanthylcyanoacetate, $[\text{O}(\text{C}_6\text{H}_4)_2\text{CH}][\text{CN}\cdot\text{CH}\cdot\text{CO}_2\text{Et}]$, forms pale green crystals melting at $124\text{--}126^\circ$ (uncorr.). T. H. P.

Grignard's Reaction. RICHARD MEYER and KARL TÖGEL (*Annalen*, 1906, 347, 55—92).—The use of Grignard's reaction in the synthesis of benzoic acid has been studied (compare Houben and Kesselkaul, *Abstr.*, 1902, i, 583; and Zelinsky, *ibid.*, 675). The action of carbon dioxide on magnesium phenyl bromide was mainly used, a trace of iodine being added as an accelerator. The influence of moisture and of temperature on the products of the reaction were studied in detail.

When magnesium is added to an ethereal solution of bromobenzene and carbon dioxide slowly passed in, benzoic acid is produced in nearly a theoretical yield, if the presence of moisture is most carefully avoided. At the same time a trace of diphenyl is always formed.

In the presence of even an extremely small quantity of water the yield of benzoic acid falls to 25 per cent., whilst that of the diphenyl rises to about 65 per cent.

If the water is introduced not at the beginning but towards the end of the reaction, a third product, benzene, is formed at the expense of the benzoic acid and the diphenyl. The percentage of benzene is in the most favourable circumstances 64, whereas that of the benzoic acid is now 20, and that of the diphenyl 45.

At temperatures above 0° other products are formed; of these the chief is triphenylcarbinol, an oil being produced at the same time from which, on fractionation under reduced pressure, benzophenone and triphenylmethane can be isolated in small quantity together with diphenyl- and triphenyl-carbinols (compare Schroeter, *Abstr.*, 1903, i, 821). In all the reactions above mentioned a trace of phenol is formed.

It is suggested that the following series of reactions takes place. In the absence of water the main reaction is represented by the equations: $\text{C}_6\text{H}_5\text{Br} + \text{Mg} = \text{C}_6\text{H}_5\cdot\text{MgBr}$; $\text{C}_6\text{H}_5\cdot\text{MgBr} + \text{CO}_2 = \text{C}_6\text{H}_5\cdot\text{CO}_2\cdot\text{MgBr}$. The diphenyl is formed probably according to the equation: $2\text{C}_6\text{H}_5\text{Br} + \text{Mg} = \text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_5 + \text{MgBr}_2$, but it is probably also produced as the result of other changes in which phenol is the first product: $\text{C}_6\text{H}_5\cdot\text{MgBr} + \text{H}_2\text{O} + \text{O} = \text{C}_6\text{H}_5\cdot\text{OH} + \text{MgBr}\cdot\text{OH}$; $\text{C}_6\text{H}_5\cdot\text{MgBr} + \text{C}_6\text{H}_5\cdot\text{OH} = \text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_5 + \text{MgBr}\cdot\text{OH}$. Hence only traces of phenol can be detected. In a special experiment, in which freshly-prepared magnesium phenyl bromide was treated with one mol. of phenol, rather more than one mol. of diphenyl was formed; prepared in this way, however, this substance could not be purified readily.

The benzene is most probably the result of the simple action of water on magnesium phenyl bromide: $\text{C}_6\text{H}_5\cdot\text{MgBr} + \text{H}_2\text{O} = \text{C}_6\text{H}_6 + \text{MgBr}\cdot\text{OH}$, a result which was tested by treating magnesium phenyl

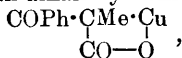
bromide with carbon dioxide in the presence of varying quantities of water. The benzophenone results from the interaction of one mol. of carbon dioxide with two mols. of magnesium phenyl bromide and subsequent decomposition of the additive product with water. The triphenylcarbinol is probably not produced directly from carbon dioxide and magnesium phenyl bromide, but from benzophenone, thus: $\text{COPh}_2 + \text{C}_6\text{H}_5 \cdot \text{MgBr} = \text{CPh}_3 \cdot \text{O} \cdot \text{MgBr} \rightarrow \text{CPh}_3 \cdot \text{OH}$, in harmony with the production of tertiary alcohols from ketones by Grignard's reaction. The triphenylmethane is probably a reduction product of the forerunner of the triphenylcarbinol.

Synthesis of the Esters of Ketonic Acids.—Unsuccessful attempts have been made to synthesise the esters of ketonic acids by the action of magnesium on a mixture of molecular proportions of an acyl chloride and halogenated ester. A magnesium-gold couple and a mercury-aluminium couple were also tried and found to be useless; but Grignard's reagent in the presence of a trace of aluminium can be used successfully if the right concentrations of ether are chosen. It is of importance to allow the magnesium to interact first with the halogenated ester.

Ethyl benzoylacetate is prepared by adding magnesium ribbon to a solution of ethyl bromoacetate in ether containing a trace of iodine. A vigorous reaction takes place as the magnesium dissolves and a thick oil separates; benzoyl bromide is now added in small portions and the mixture heated. The ethyl benzoylacetate is then converted into the sodium derivative and after acidification extracted with ether.

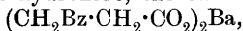
Benzoylacetic acid is obtained from the ester by hydrolysing by Ceresole's method; the acid melts and decomposes at $100-101^\circ$. Ethyl benzoylacetate was also prepared, but with a less satisfactory yield, from ethyl chloroacetate and benzoyl chloride in the presence of aluminium and magnesium.

Ethyl α -benzoylpropionate, similarly prepared from ethyl α -bromopropionate and benzoyl bromide, boils at $100-102^\circ$ under 48 mm. pressure. The *copper* salt is a green powder decomposing at 180° and readily soluble in organic solvents. If the ester is treated with copper acetate in the presence of an alkali hydroxide, the *copper* salt,



is produced. Attempts to obtain α -dibenzoylpropionic acid and tribenzoylacetic acid led to no results. When ethyl α -benzoylpropionate is hydrolysed, only benzoic and propionic acids are isolated.

Ethyl β -benzoylpropionate, obtained by the method above described from ethyl β -iodopropionate and benzoyl bromide, crystallises in leaflets, melts at 19° , and boils at $183-184^\circ$ under 22 mm. pressure. When hydrolysed with barium hydroxide, the *barium* salt,



is obtained and crystallises in small needles. From the latter, the acid can be easily prepared. β -Dibenzoylpropionic acid, obtained by the action of benzoyl chloride on ethyl β -benzoylpropionate in the presence of sodium ethoxide, melts at 194° and gives a red coloration with ferric chloride.

Ethyl acetoacetate is prepared from ethyl bromoacetate and acetyl chloride.

Attempts to condense ethyl *m*-bromobenzoate with benzoyl bromide failed.

K. J. P. O.

Pechmann's Dye [from Benzoylacrylic Acid]. I. TAD. KÓZ-
NIEWSKI and LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1906,
81—95).—Homologues of benzoylacrylic acid have been prepared by
condensing aromatic hydrocarbons with maleic anhydride in the presence
of aluminium chloride. The *phenylhydrazone* of benzoylacrylic acid,
 $C_{16}H_{14}O_2N_2$, crystallises from benzene in golden-yellow needles and
melts at 197° . The *methyl ester* of the acid, $COPh \cdot CH : CH \cdot CO_2Me$,
forms pale yellow needles melting at $30-32^\circ$, and boiling at 185°
under 16 mm. pressure.

m-Xyloylacrylic acid, $C_6H_3Me_3 \cdot CO \cdot CH : CH \cdot CO_2H$, is best prepared
at low temperatures, and melts at 114° . *Phenetoxyacrylic acid*,
 $OEt \cdot C_6H_4 \cdot CO \cdot CH : CH \cdot CO_2H$, melts at $143-144^\circ$; *ψ-cumoylacrylic*
acid, $C_6H_2Me_3 \cdot CO \cdot CH : CH \cdot CO_2H$, melts at 149° , and the isomeric
mesitoxyacrylic acid at 140.5° .

Each acid yields a dye corresponding with Pechmann's dye from
benzoylacrylic acid (Abstr., 1882, 1074) when warmed with dehydrating
agents, especially acetic anhydride. The yields in most cases are poor.
A better yield of dye appears to be formed when the benzoylacrylic
acid contains γ -keto- α -hydroxyphenylbutyric acid, due to admixture of
maleic anhydride with the maleic anhydride. The dye from mesitoxy-
acrylic acid is more readily soluble in chloroform or xylene than its
homologues, and its solutions are coloured reddish-yellow, and possess
a somewhat different absorption spectrum.

When oxidised, the dye from benzoylacrylic acid yields benzoic, and
that from toluylacrylic acid, terephthalic acid. The dye from benzoyl-
acrylic acid reacts with aniline and acetic acid, yielding a *dianilide*,
 $C_{32}H_{22}O_2N_2$, which crystallises in dark green, glistening needles soluble
in xylene to a deep purple solution. Both alcoholic potassium
hydroxide and bromine react with Pechmann's dye, for which the
formula $COPh \cdot C \begin{smallmatrix} \swarrow CO \cdot CH \\ \searrow CH \cdot CO \end{smallmatrix} C \cdot COPh$ is suggested.

J. J. S.

Hippocoprosterol. GERSON GITTELMACHER-WILENKO (*Bull. Acad.*
Sci. Cracow, 1906, 20—23).—Bondzyński and Humnicki's hippocopro-
sterol (Abstr., 1897, i, 183) consists of two compounds.

α -Hippocoprosterol, $C_{27}H_{54}O$ or $C_{27}H_{52}O$, dissolves readily in 97 per
cent. alcohol, crystallises in slender, rhombic plates resembling chole-
sterol, and melts at $66-67^\circ$. It gives Salkowski's and Liebermann's
reactions but feebly.

β -Hippocoprosterol, $C_{27}H_{52}O$ or $C_{27}H_{50}O$, is almost insoluble in cold
alcohol, separates as a gelatinous mass of minute needles, and melts
at 56° .

J. J. S.

β -Nitroisoapioles. ENRICO RIMINI and F. OLIVARI (*Atti R. Accad.*
Lincei, 1906, [v], 15, ii, 138—141).—Dill *isoapiole nitrosite*, $C_{12}H_{14}O_2N_2$,
prepared by a method analogous to that used for obtaining *isomyristicin*

nitrosite (compare Rimini, Abstr., 1905, i, 656), is a lemon-yellow powder melting and decomposing at about 134° . The corresponding β -nitroisopiole, $C_{12}H_{13}O_6N$, separates from alcohol in yellow crystals and melts at $94-95^{\circ}$.

The isomeric β -nitroisopiole, obtained from parsley oil, crystallises from alcohol in silky, yellow needles melting at 96° . The bromo-derivative, $C_6Br(O_2CH_2)(OMe)_2 \cdot CH:Me \cdot NO_2$, crystallises from alcohol in yellow laminae melting at 120° . On treatment with hydroxylamine (1 mol.), this β -nitroisopiole, in aqueous-alcoholic solution, gives *apiolaldoxime*, $C_{11}H_{10}O_6N$, melting at 160° .

In the preparation of β -nitroisomyristicin (*loc. cit.*), myristicinaldehyde is also formed, and in that of β -nitroisopiole from parsley oil, apiolaldehyde is obtained in small quantity. T. H. P.

Bixin. The Colouring Matter of Bixa Orleana. I. LEON MARCHLEWSKI and LAD. MATEJKO (*Bull. Acad. Sci. Cracow*, 1905, 745—753. Compare Etti, *Ber.*, 1878, 11, 864; Zwick, Abstr., 1897, i, 630).—Bixin crystallises from a mixture of chloroform and alcohol or from glacial acetic acid in dark red rhomboids melting at 198° when heated quickly, or at 191.5° when slowly heated. Its solubility in chloroform at 25° is 0.34 gram per 100. The analyses agree with Etti's formula, $C_{28}H_{34}O_5$. Its spectra in chloroform and alcoholic solutions are similar to those of lipochrom (*Proc. Roy. Soc.*, 1898, 63, 389; 1899, 65, 177). Monosodium and potassium salts have been prepared. Bixin contains one methoxyl group, and although it possesses distinct acidic properties, definite alkyl derivatives could not be prepared. When reduced with zinc dust and acetic acid, bixin yields an orange product melting at 200.5° . It rapidly changes when exposed to the air at 100° and becomes colourless. J. J. S.

Tannins. II. Eutannin. HERMANN THOMS (*Chem. Centr.*, 1906, i, 1829—1830; from *Apoth.-Zeit.*, 21, 354—356. Compare this vol., ii, 504).—Commercial eutannin, free from lactose, is found to be identical with chebulinic acid, $C_{78}H_{22}O_{19}$. It crystallises from water in small, colourless needles containing H_2O and decomposing at 234° , and dissolves readily in alcohol, acetone, ethyl acetate, or amyl alcohol, sparingly in chloroform or light petroleum. It reacts acid towards litmus and has $[\alpha]_D$ initially $+61.7^{\circ}$, gradually rising to $+66.9^{\circ}$. It forms an *ennea-acetyl* derivative and a *methyl* derivative, the latter yielding trimethylgallic acid when treated with concentrated sodium hydroxide solution. When heated with water at $100-150^{\circ}$, eutannin yields gallic acid and *eutannin hydrate*, $C_{78}H_{24}O_{20}$, which is a white, amorphous powder decomposing at $200-210^{\circ}$; it dissolves readily in water, alcohol, acetone, or ethyl acetate and moderately in ether.

On dissolving eutannin in cold dilute sodium hydroxide solution in absence of air and subsequently acidifying with acetic acid and adding lead acetate solution, a precipitate is formed which, when treated with hydrogen sulphide, yields gallic acid and a *decomposition-tannin*, $C_{14}H_{16}O_{12}$ or $C_{14}H_{14}O_{11}$, as a pale yellow, amorphous powder, soluble in water, alcohol, acetone, ethyl acetate, or ether; it decomposes at about 260° , has $[\alpha]_D +26^{\circ}$ at 15° , gives a blue coloration with ferric chloride,

reduces Fehling's solution slightly, has an acid reaction towards litmus, and yields a white precipitate with quinine salts.

Probable formulæ are suggested for the above compounds.

T. H. P.

Quebracho Tannin. II. MAXIMILIAN NIERENSTEIN (*Chem. Centr.*, 1906, i, 1893; from *Collegium*, 1906, 141—142. Compare this vol., i, 446).—One gram of quebracho-tannin, either alone or with 100 grams of sodium acetate (compare Perkin and Yoshitake, *Trans.*, 1902, 81, 1164), is dissolved in 500 c.c. of water, and to the well-cooled solution 0.5 per cent. diazobenzene chloride solution is added, drop by drop, until a permanent turbidity appears. After twenty-four hours, the deposit formed is repeatedly extracted with boiling acetone. An amorphous product is thus obtained which melts above 360°, is insoluble in alcohol and other solvents, and gives, on analysis, the numbers: (1) C, 52.2; H, 3.18; and N, 14.55 per cent., when prepared without sodium acetate; and (2) C, 52.55, 54.40, and 59.90; H, 2.97, 3.18, and 4.00; N, 13.17, 14.50, and 14.55 per cent., when prepared by Perkin and Yoshitake's method. On boiling the azo-compound for forty hours with absolute alcohol and evaporating, there remains an amorphous, red, optically inactive residue, which dissolves in water or alcohol, gives all the reactions of a catechol-tannin, and contains 56.6 per cent. of carbon and 3.2 of hydrogen. This result tends to confirm the author's view (*Abstr.*, 1905, i, 914) that the activity of the colouring matter may depend on the sugar which accompanies it.

T. H. P.

Derivatives of Dihydroisobenzofuran. Parts I to III. ALFRED GUYOT and J. CATEL (*Bull. Soc. chim.*, 1906, [iii], 35, 551—562, 562—567, 567—571).—Most of the facts recorded in these papers have been published previously (*Abstr.*, 1905, i, 226, 516, 540). 2-Hydroxy-1:1:2-triphenyl-1:2-dihydroisobenzofuran (*Abstr.*, 1905, i, 226) separates from carbon disulphide in splendid crystals belonging to the monoclinic system, and is soluble in most organic solvents. *o*-Benzhydryltriphenylcarbinol (*loc. cit.*), produced by reducing the foregoing with sodium amalgam, when warmed in acetic acid solution with hydrochloric acid gives 1:1:2-triphenyl-1:2-dihydroisobenzofuran, $C_6H_4 \begin{smallmatrix} \text{CPh}_2 \\ \text{CHPh} \end{smallmatrix} O$, which crystallises from boiling alcohol in leaflets and melts at 120°. On oxidation with chromic acid, it is re-converted into the parent hydroxytriphenylisobenzofuran, and, like the latter, yields 9:10-diphenylanthracene when heated with sulphuric acid.

1:1-Diphenyl-1:2-dihydroisobenzofuran (*Abstr.*, 1905, i, 517) separates from organic solvents in colourless leaflets and melts at 93°.

T. A. H.

Constitution of Hordenine. EUGÈNE LÉGER (*Compt. rend.*, 1906, 143, 234—236. Compare this vol., i, 204).—The oxidation of hordenine by either alkaline or acid potassium permanganate or chromic acid yields only oxalic acid, whilst, when nitric acid is employed, picric acid is also obtained.

Hordenine methiodide, when treated with silver hydroxide, yields the methoxide, which, on distillation in an oil-bath, gives trimethylamine; a dense, colourless oil, having an agreeable aromatic odour and volatile in a current of steam; and an amorphous, phenolic compound non-volatile at 180—190°.

On the basis of these results, the author suggests the formula $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_2$ for hordenine. T. H. P.

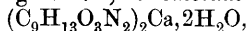
Meroquinenine and the Constitution of the Cinchona Alkaloids. WILHELM KOENIGS (*Annalen*, 1906, 347, 143—232).—The introduction to this paper contains a complete historical account of the investigations on the alkaloids of the cinchona bark. The researches which bear on the constitution of these alkaloids are discussed at length.

[With KARL BERNHART and JOSEF IBELE.]—Of the methods of preparing meroquinenine, namely, the hydrolysis of cinchenine with phosphoric acid, the hydrolysis of quinine, and the oxidation of cinchonine with chromic acid, the last mentioned is the most effective.

Pure meroquinenine melts and decomposes at 223—224° and has $[\alpha]_D = 27.58$ —27.9° at 20° in a 10 per cent. aqueous solution (compare Abstr., 1894, i, 477). The *hydrochloride* forms colourless crystals melting at 146—148°, and the *aurichloride*, yellow needles which melt and decompose at 142°. The *monomethyl ether*, $\text{C}_9\text{H}_{14}\text{O}_2\text{NMe}$, prepared from the alkaloid and methyl alcohol in the presence of sulphuric acid, is a colourless oil which yields a crystalline *hydrochloride*; the *hydrochloride* of the *ethyl ether* crystallises in needles melting at 165°.

Meroquinenine yields an *acetyl* derivative, $\text{C}_9\text{H}_{14}\text{O}_2\text{NAc}$, which crystallises in plates melting at 110°; it still possesses faint basic properties, but at the same time has marked acid properties and yields a *silver* salt. The *ethyl* ester of the acetyl derivative is an oil.

Nitrosomeroquinenine, $\text{C}_9\text{H}_{14}\text{O}_2\text{N} \cdot \text{NO}$, prepared from the alkaloid and sodium nitrite in the presence of dilute sulphuric acid, forms colourless crystals melting at 67°; its *calcium* salt,

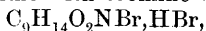


by means of which it is purified, is a soluble crystalline powder. The markedly acid properties of the acetyl and nitroso-derivatives show the presence of a carboxyl group, which is masked in the original alkaloid by the amino-group.

When meroquinenine is oxidised by a mixture of chromic and sulphuric acids, cincholeuponic acid is mainly formed, together with formic acid. When reduced with fuming hydriodic acid, meroquinenine is converted into cincholeupone, $\text{C}_9\text{H}_{17}\text{O}_3\text{N}$.

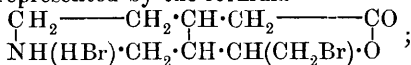
When meroquinenine is vigorously reduced with hydriodic acid and red phosphorus, 2-methyl-3-ethylpyridine is formed; the *picrate* crystallises in needles melting at 148—150°, and the *aurichloride* in yellow needles melting at 138°; when oxidised with permanganate, a mixture of 3:4-pyridinedicarboxylic and 4-methylpyridine-3-carboxylic acids is produced, the constitution of the pyridine being thus demonstrated.

On treating meroquinenine with bromine water, a compound,



is formed, which can be reduced by zinc dust and sulphuric acid to meroquinenine. This *hydrobromide* yields a nitroso-derivative,

$C_9H_{13}O_2NBr \cdot NO$,
forming colourless crystals melting at 98° (compare Koenigs and Comstock, Abstr., 1884, 1382), which has, however, no acid properties, and is probably represented by the formula



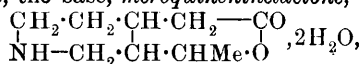
in the action of the bromine water, the halogen is first of all added to the ethylene linking, and then one bromine atom eliminated with the hydrogen of the carboxyl group, a lactone ring being formed.

Hydroxymeroquinenine, $C_9H_{14}O_2N \cdot OH$, is obtained as a hydrochloride by boiling the hydrobromide just described with an aqueous suspension of silver chloride; it crystallises with H_2O and melts and decomposes at 254° ; the *hydrochloride* crystallises in needles melting and decomposing at $208\text{--}210^\circ$, and yields a *platinichloride* decomposing at 240° ; the *aurichloride* crystallises in needles, melting and decomposing at 184° . A *monoacetyl* derivative was obtained by heating the hydroxy-compound with acetic anhydride and isolated as an *aurichloride*, $C_{11}H_{17}O_4N \cdot HAuCl_4$, which melts and decomposes at 214° . Attempts to esterify hydroxymeroquinenine were unsuccessful.

When the ethyl ester of meroquinenine is treated with ethyl iodide, the *ethyl ester of N-ethylmeroquinenine hydriodide*, $C_9H_{13}NEtO_2Et \cdot HI$, is obtained as colourless needles melting at $156\text{--}157^\circ$; by treatment with silver chloride it can be converted into the corresponding *hydrochloride*, which crystallises in colourless prisms melting at $220\text{--}221^\circ$; the corresponding *hydrobromide* melts at 194° . When boiled with aqueous hydrochloric acid, these esters are hydrolysed and the *hydrochloride* of *N*-ethylmeroquinenine, $C_{11}H_{19}O_2N \cdot HCl$, which melts at 165° , is produced. The base could not be obtained in a crystalline form. When the hydrobromide of the ethyl ester of *N*-ethylmeroquinenine is treated with bromine in chloroform solution, two atoms of bromine are added on at the ethylene linking, and the compound $CH_2 \text{---} CH_2 \cdot CH \cdot CH_2 \cdot CO_2Et$ is produced; it crystallises in $NEt(HBr) \cdot CH_2 \cdot CH \cdot CHBr \cdot CH_2Br$

colourless needles, melting and decomposing at 182° . When hydrolysed by boiling dilute hydrobromic acid, the *hydrobromide* of *N*-ethylbromomeroquinenine, $CH_2 \text{---} CH_2 \cdot CH \cdot CH_2 \text{---} CO$ is formed, a $NEt(HBr) \cdot CH_2 \cdot CH \cdot CH(CH_2Br) \cdot O$, lactone ring at the same time appearing; it crystallises in colourless needles melting and decomposing at $218\text{--}220^\circ$.

When meroquinenine is heated with a concentrated solution of arsenic acid at $180\text{--}190^\circ$, oxidation does not occur, but the elements of water are added, a hydroxydihydromeroquinenine being formed; when treated with hydrochloric acid, water is again eliminated, a *hydrochloride* melting and decomposing at $255\text{--}256^\circ$ being produced, which is isomeric with the hydrochloride of meroquinenine. From this hydrochloride, the base, *meroquineninelactone*,



or *hydroxydihydromeroquinenine*, can be prepared, and crystallises in colourless prisms melting and decomposing at 220°. When the hydrochloride is treated with bromine or iodine and sodium hydroxide, bromoform and iodoform are respectively produced, reactions which indicate the presence of a methyl group as in the above formula.

On heating meroquinenine with hydrochloric acid, a meroquinenine lactone is not produced in any quantity, but the major portion of the base is converted into a levorotatory base, the *platinichloride* of which crystallises in yellow needles or leaflets melting and decomposing at 232°.

K. J. P. O.

The Relations between Functional (Reactive) Groups in Remote Positions. Decamethyleneimine. EDMOND E. BLAISE and L. HOUILLON (*Compt. rend.*, 1906, 143, 361—363. Compare this vol., i, 692).—By the action of heat on decamethylenediamine hydrochloride, a mixture of bases is obtained which contains a small quantity of 2-hexylpyrrolidine; the *platinichloride*, *aurichloride*, and *carbamide* of this base melt at 117°, 85°, and 146° respectively, and are identical with the corresponding derivatives of 2-hexylpyrrolidine prepared synthetically by a similar method to that adopted in the synthesis of 2-butylpyrrolidine (*loc. cit.*).

ε-Aminodecoic acid, $\text{CO}_2\text{H}\cdot[\text{CH}_2]_8\cdot\text{CH}_2\cdot\text{NH}_2$, prepared from brassylamic acid, $\text{CO}_2\text{H}\cdot[\text{CH}_2]_9\cdot\text{CO}\cdot\text{NH}_2$, can be crystallised from hot water and melts at 187—188°; the *hydrochloride* crystallises from hot water, and the *benzoyl* derivative crystallises from dilute alcohol in small nodules and melts at 97°. The properties of *ε*-aminodecoic acid and its derivatives thus prepared are quite different from those ascribed by Krafft to the *ε*-aminodecoic acid prepared from his so-called decamethyleneimine (Krafft and Phookan, *Abstr.*, 1892, 1180). It is probable, therefore, that decamethyleneimine does not exist, and that the reaction between functional groups in the same molecule is not a periodic function of the position of these groups.

M. A. W.

Preparation of Pure Piperidine. DANIEL VORLÄNDER and THEODOR WALLIS (*Annalen*, 1906, 345, 277—288. Compare this vol., i, 729, 730).—The velocity of oxidation of the purest commercial piperidine is so great, in comparison with that of diethylamine, as to render probable the occurrence of easily oxidisable impurities in the former. A purification can be effected by twice shaking an aqueous solution of piperidine (125 grams per litre) and sulphuric acid (250 grams per litre) with 70 grams of powdered potassium permanganate, the first time for ten minutes and the second time, with the recovered piperidine, for two to three hours. A better method is to treat nitrosopiperidine in acetone with solid permanganate for one to two days in the cold, or for three to four hours at a higher temperature. The piperidine recovered from the nitroso-compound in toluene by hydrogen chloride has a constant velocity of oxidation; the acetyl derivative boils at 223°, the hydrochloride melts at 245° (corr.), and the platinichloride at 201·5° (corr.).

From the precipitate obtained from the acetone solution during the oxidation, a dibasic *nitroso-acid* can be isolated, having the composition

$C_3H_6ON_2(CO_2H)_2$, melting at 79° , and showing Liebermann's reaction. A neutral, colourless, crystalline substance, $C_5H_{10}O_2NCl$ or $C_5H_{12}O_2NCl$, was also isolated; it melts at 212° and yields ethyl acrylate when heated. The presence of a partially hydrogenated pyridine in commercial piperidine was also indicated by the behaviour of acetylpiperidine towards bromine. The crude substance reacts with bromine to the extent of 17.5 per cent., whereas the acetyl compound obtained from purified piperidine does not react at all.

The oxidation velocity of other secondary amines, purified in a similar manner, is only slightly changed, except in the case of dipropylamine, the constant for which falls to about one-quarter of its original value. C. S.

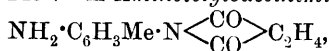
Transformation of Quinoline into 2-Methylindole. MAURICE PADOA and A. CARUGHI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 113—118. Compare this vol., i, 530, 695).—When a mixture of quinoline vapour and hydrogen is passed through a tube containing reduced nickel at a temperature of 260 — 280° , one part of the quinoline is converted into 2-methylindole and, after the opening of the closed nucleus, the remainder in part loses one carbon atom and in part two carbon atoms, giving rise to methyl-*o*-toluidine and *o*-toluidine. No methylindoline is formed in the reaction. T. H. P.

Ring-formation. II. RICHARD MEYER (*Annalen*, 1906, 347, 17—54. Compare Abstr., 1903, i, 442).—The investigation of the action of dibasic acids on *o*-, *m*-, and *p*-diamines has been continued. [With G. VON LUTZAU.]—Malonanilide is readily obtained from aniline and excess of ethyl malonate. α -Malon-naphthil, $C_{10}H_7N \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} CH_2$, is formed when α -naphthylamine and ethyl malonate are heated for some hours. It crystallises in needles, melts above 300° , and is soluble in alkali hydroxides (compare Whiteley, Trans., 1903, 83, 24).

o-Phenylenemalonamide, prepared from *o*-phenylenediamine hydrochloride and the calculated quantity of sodium carbonate in presence of excess of ethyl malonate, crystallises in needles melting above 300° . The corresponding derivative of *o*-tolylenediamine crystallises in needles melting above 300° . No definite product could be obtained from *m*-phenylenediamine and ethyl malonate, but *m*-tolylenediamine [Me : $(NH_2)_2 = 1 : 2 : 4$] and ethyl malonate yield ethyl *m*-tolylenedimalonamate, $C_6H_3Me(NH \cdot CO \cdot CH_2 \cdot CO_2Et)_2$, which is a white, amorphous powder melting at 110 — 113° . *p*-Phenylenediamine and ethyl malonate yield the similarly constituted compound, $C_6H_4(NH \cdot CO \cdot CH_2 \cdot CO_2Et)_2$, which crystallises in needles and melts at 164° .

Aniline and ethyl succinate yield succinanil, similarly α -naphthylamine yields α -succinonaphthil, but β -naphthylamine gives the ester of ethyl β -naphthylsuccinamate, $C_{10}H_7NH \cdot CO \cdot C_2H_4 \cdot CO_2Et$, which crystallises in needles and melts at 99 — 100° . The condensation products prepared from *o*-phenylenediamine or *o*-tolylenediamine and ethyl succinate could not be purified satisfactorily. From *m*-phenylenediamine and ethyl succinate, a compound is obtained, crystallising in

needles and melting at 205° , the chemical nature of which could not be established; with ammonia it yields *m*-phenylenedisuccinamide, $C_6H_4(NH \cdot CO \cdot C_2H_4 \cdot CO \cdot NH_2)_2$, which crystallises in needles melting and decomposing at 245° . *m*-Aminotolylsuccinimide,



is formed from *m*-tolylenediamine and crystallises in needles melting at $256-259^{\circ}$. *p*-Phenylenediamine yields *p*-aminosuccinanil (*loc. cit.*).

[With P. JAEGER.]—With ethyl isosuccinate, the diamines yield similar compounds. *o*-Phenyleneisosuccinimide, $C_6H_4 \begin{array}{c} \diagup NH \cdot CO \\ \diagdown NH \cdot CO \end{array} CHMe$, crystallises in yellow plates, melting above 350° ; at the same time, a base, $CHMe(CO \cdot NH \cdot C_6H_4 \cdot NH_2)_2$, which is purified in the form of a *picrate*, is produced; the latter crystallises in yellow plates and melts and decomposes at $245-250^{\circ}$; the base, which could not be purified, crystallises in slender needles.

m-Phenylenediamine and ethyl isosuccinate yield an insoluble compound melting at $275-280^{\circ}$. From *p*-phenylenediamine, ethyl *p*-phenylenediisuccinamate, $C_6H_4(NH \cdot CO \cdot CHMe \cdot CO_2Et)_2$, is formed. It crystallises in needles and melts at $180-181^{\circ}$. The condensation product from *m*-tolylenediamine could not be isolated in the pure state. *o*-Tolylenediamine yields similarly a mixture of *o*-tolyleneisosuccinamide and the basic *di-o*-aminotolylsuccinamide, which are separated by treatment with dilute acetic acid; the former crystallises in needles or plates, the latter in needles, and yields a *picrate* which crystallises in yellow needles melting and decomposing at $235-240^{\circ}$.

Ethyl adipate reacts with *o*-phenylenediamine, yielding in small amount a basic, crystalline substance which could not be purified.

[With JOH. MAIER.]—Ethyl sebacate yields with *o*-phenylenediamine two compounds: *o*-phenylenesebacamide, $C_6H_4 \begin{array}{c} \diagup NH \cdot CO \\ \diagdown NH \cdot CO \end{array} C_8H_{16}$, crystallises in needles melting at $134-135^{\circ}$, and is indifferent towards both acids and bases. *Di-o*-aminophenylsebacamide,

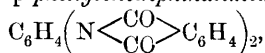
$C_8H_{16}(CO \cdot NH \cdot C_6H_4 \cdot NH_2)_2$, crystallises in needles melting above 320° . Ethyl *m*-phenylenedisebacate, $C_6H_4(NH \cdot CO \cdot C_8H_{16} \cdot CO_2Et)_2$, is prepared by the condensation of *m*-phenylenediamine with the ester, and crystallises in microscopic needles melting at 97° ; at the same time a yellow, insoluble powder is formed. *p*-Phenylenediamine and ethyl sebacate yield several products, of which *p*-aminosebacanil, $NH_2 \cdot C_6H_4 \cdot N \begin{array}{c} \diagup CO \\ \diagdown CO \end{array} C_8H_{16}$, can be isolated; it crystallises in needles melting at $150-151^{\circ}$.

[With P. JAEGER.]—The condensations of the chlorides of dibasic acids with aromatic diamines have been investigated. With succinyl chloride, *o*-phenylenediamine yields *di-o*-aminophenylsuccinamide, whilst *m*-phenylenediamine and *p*-phenylenediamine do not give condensation products, but merely succinates of the base. With *o*-tolylenediamine, *di-o*-aminotolylsuccinamide, $C_2H_4(CO \cdot NH \cdot C_6H_3Me \cdot NH_2)_2$, is formed, and crystallises in needles melting above 320° ; the hydrochloride was analysed.

Adipic chloride and *o*-phenylenediamine yield *di-o*-aminophenyl-

adipamide, which was isolated as *hydrochloride*; the latter crystallised in long needles.

From phthalyl chloride and *o*-phenylenediamine, *di-o-aminophenyl-phthalamide*, $\text{C}_6\text{H}_4(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$, was prepared as colourless needles. At the same time, *o*-phenylenephthalamide was formed, and also *o*-phenylenediphthalamide, the latter being generally the main product of the reaction. Phthalyl chloride and *o*-tolylenediamine gave *o*-tolylenediphthalamide. Phthalyl chloride and *p*-phenylenediamine yield *p*-aminophthalanil and *p*-phenylenediphthalamide,



which crystallises in needles or in rhombic plates and melts at 356° .

K. J. P. O.

Constitution of Nitroimines and Action of Phenylcarbimide on Methylnitroamine. ROLAND SCHOLL (*Annalen*, 1906, **345**, 363—384. Compare Abstr., 1905, i, 181; Angelucci, *ibid.*, i, 801; Angeli and Castellana, this vol., i, 162).—In addition to the evidence adduced previously (*loc. cit.*), the following arguments are advanced in

favour of the nitroimine formula, $\text{>CH}\cdot\text{C}\cdot\text{N}\cdot\text{NO}_2$. (1) The behaviour of the nitroimines towards alkalis resembles that of secondary nitroamines. (2) The fact that the nitroimines are pseudo-acids and yield *N*- and *O*-alkyl derivatives cannot be brought into line with Angeli and Castellana's "pernitroso" formula. (3) Reducing agents generally eliminate an atom of nitrogen; in some cases, however, hydrazine derivatives are obtained. (4) Nitroimines, as a class, give the Thiele-Lachmann nitroamine reaction; the nitroimines obtained from the oximes of pinacolin, santonin, menthone, and mesityl oxide give, like most nitroamines, the Liebermann reaction. Camphornitroimine gives colour reactions with phenol and sulphuric acid, but the author does not assert positively that these are due to Liebermann's reaction. (5) The occurrence of camphanazine, nitrogen, camphene, and camphor-oxime among the reduction products of camphornitroimine can be explained rationally by the nitroimine formula, and does not require the assumption of the existence of the otherwise quite unknown "pernitroso" group.

[With KARL HOLDERMANN.]— α -Nitro- β -phenyl- α -methylcarbamide, $\text{NHPh}\cdot\text{CO}\cdot\text{N}(\text{NO}_2)\text{Me}$, is obtained by the reaction of methylnitroamine and "active" phenylcarbimide (phenylcarbimide containing phenylcarbamate), dry ether being added when the temperature rises to 35 — 40° . With ordinary phenylcarbimide the reaction proceeds slowly, but more rapidly after the addition of a small quantity of carbamide. The colourless crystals, after the removal of *s*-diphenylcarbamide by acetone and light petroleum, sinter at 68° and melt and decompose at $74\cdot5$ — 75° . It gives Liebermann's reaction, is decomposed by boiling water, and with ammonia (or aniline) in ether at the ordinary temperature yields phenylcarbamide (or diphenylcarbamide) and methylnitroamine.

s-Nitrophenylmethylcarbamide, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NHMe}$, results from the action of ethyl nitrate on *s*-phenylmethylcarbamide in concentrated sulphuric acid at -5° . The yellow product is boiled with one

per cent. sodium hydroxide, cooled, and the residue crystallised from hot acetic acid. The substance forms colourless prisms, becomes yellow at 190—200°, and melts at 230—231°. Hot dilute sodium hydroxide solution dissolves it to a yellow solution, from which the substance is recovered unchanged on cooling. The presence of the nitro-group in the benzene nucleus is deduced from the fact that the substance gives neither the Liebermann nor the Thiele-Lachmann nitroimine reaction.

s-Dinitrophenylmethylcarbamide, $C_6H_3(NO_2)_2 \cdot NH \cdot CO \cdot NHMe$, results when twice the quantity of ethyl nitrate is used in the preceding preparation; it forms yellow needles, melts and decomposes at 206—207°, and resembles the preceding compound in its behaviour. C. S.

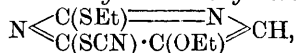
Constitution of Scholl's Nitroimines. OTTORINO ANGELUCCI (*Gazzetta*, 1906, **36**, i, 627—628. Compare Abstr., 1905, i, 801).—The author criticises the work of Scholl (preceding abstract), who states that the nitroimines react with secondary amines according to the equation $:C:N \cdot NO_2 + NH_2R = :C:NR + H_2NO_2 \rightarrow H_2O + N_2O$. In the cold, however, camphornitroimine reacts with methylamine, giving water and nitrous oxide, which products cannot be regarded as derived from the decomposition of the nitroamide, since this is stable under the conditions of the experiment.

Further, Scholl states that all nitroimines give the reaction of Liebermann and that of Thiele and Lachmann. The author finds that pernitrosocamphor gives no trace of Liebermann's reaction.

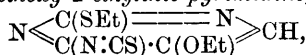
T. H. P.

Benzenesulphomethylguanidine. D. ACKERMANN (*Zeit. physiol. Chem.*, 1906, **48**, 382. Compare this vol., ii, 505).—Methylguanidine reacts with benzenesulphonic chloride yielding *benzenesulphomethylguanidine*, which melts at 184°; its solubility in water at the ordinary temperature is 0.04 in 100. J. J. S.

Pyrimidines: Action of Potassium Thiocyanate on Imide Chlorides. XV. TREAT B. JOHNSON and ELMER V. MCCOLLUM (*Amer. Chem. J.*, 1906, **36**, 136—148. Compare this vol., i, 704; Wheeler and Merriam, Abstr., 1901, i, 514; Wheeler and Bristol, Abstr., 1905, i, 483).—6-Thiocyano-5-ethoxy-2-ethylthiolpyrimidine,

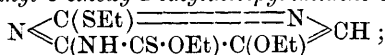


prepared by boiling 6-chloro-5-ethoxy-2-ethylthiolpyrimidine with potassium thiocyanate in 95 per cent. alcoholic solution, crystallises from alcohol in lemon-yellow prisms, melts at 66—67°, and dissolves in concentrated hydrochloric acid, being reprecipitated by alkali hydroxides or on dilution. It reacts with thiobenzoic or thioacetic acid with development of heat, forming 6-thio-5-ethoxy-2-ethylthiolpyrimidine, $NH \begin{array}{c} \diagup C(SEt) \\ \diagdown CS \cdot C(OEt) \end{array} \begin{array}{c} \text{---} N \\ \text{---} N \end{array} \begin{array}{c} \diagdown \\ \diagup \end{array} CH$, which is prepared also by boiling 6-chloro-5-ethoxy-2-ethylthiolpyrimidine with alcoholic potassium sulphide; it crystallises from alcohol in yellow prisms and melts at 144—145°.

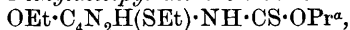
6-Thiocarbimido-5-ethoxy-2-ethylthiolpyrimidine,

is formed when the 6-thiocyanopyrimidine is heated at 105—110°; it solidifies over concentrated sulphuric acid, melts at 45—50°, boils at 228—235° under 20—23 mm. pressure, is exceedingly hygroscopic, and when treated with ammonia yields *6-thiocarbamido-5-ethoxy-2-ethylthiolpyrimidine*, $\text{N} \begin{array}{c} \diagup \text{C(SET)} \\ \diagdown \text{C(NH}\cdot\text{CS}\cdot\text{NH}_2) \cdot \text{C(OEt)} \end{array} \text{N} \text{---} \text{CH}$, which crystallises from alcohol in yellow prisms and melts at 172°.

When 6-chloro-5-ethoxy-2-ethylthiolpyrimidine is boiled with potassium thiocyanate in alcoholic solution, the cyanthiol formed changes slowly into the thiocarbimido-derivative, which reacts with alcohol, forming *ethyl 5-ethoxy-2-ethylthiolpyrimidine-6-thiocarbamate*,

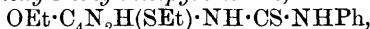


this crystallises in long prisms, melts at 93—94°, volatilises to some extent when evaporated with alcohol, and is soluble in aqueous sodium hydroxide.

n-Propyl 5-ethoxy-2-ethylthiolpyrimidine-6-thiocarbamate,

formed similarly by boiling 6-chloro-5-ethoxy-2-ethylthiolpyrimidine with potassium thiocyanate in *n*-propyl-alcoholic solution, crystallises in small prisms and melts at 56—57°.

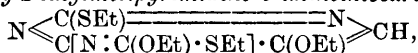
The following thiocarbamido-derivatives are prepared by heating 6-thiocyano-5-ethoxy-2-ethylthiolpyrimidine at 150—160° and treating the product with the aromatic base in benzene solution. *6-Phenylthiocarbamido-5-ethoxy-2-ethylthiolpyrimidine*,



forms distorted prisms and melts at 82—83°. *6-p-Tolylthiocarbamido-5-ethoxy-2-ethylthiolpyrimidine*, $\text{C}_{16}\text{H}_{20}\text{ON}_4\text{S}_2$, forms stellate clusters of needles and melts at 115°. *6-o-Tolylthiocarbamido-5-ethoxy-2-ethylthiolpyrimidine*, $\text{C}_{16}\text{H}_{20}\text{ON}_4\text{S}_2$, crystallises in rhombic prisms and melts at 129—130°. *6-p-Anisylthiocarbamido-5-ethoxy-2-ethylthiolpyrimidine*, $\text{OEt} \cdot \text{C}_4\text{N}_2\text{H(SET)} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, crystallises from alcohol in rhombic prisms and melts at 122—123°. *6-m-Nitrophenylthiocarbamido-5-ethoxy-2-ethylthiolpyrimidine*, $\text{C}_{15}\text{H}_{17}\text{O}_3\text{N}_5\text{S}_2$, forms slender prisms and melts at 161°. G. Y.

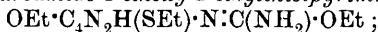
Pyrimidines: Formation of Purines from Carbamido-pyrimidines. XVI. TREAT B. JOHNSON and ELMER V. MCCOLLUM (*Amer. Chem. J.*, 1906, **36**, 149—159. Compare preceding abstract and this vol., i, 704).—*Ethyl formylglycollate*, $\text{OEt} \cdot \text{CH}(\text{COH}) \cdot \text{CO}_2\text{Et}$, is obtained on addition of hydrochloric acid to its sodium salt as a colourless oil which boils at 115—118° under 35 mm. pressure.

2:6-Dioxy-5-ethoxypyrimidine is readily prepared by boiling 5-ethoxy-2-methylthiolpyrimidine with hydrochloric acid.

Ethyl 5-ethoxy-2-ethylthiolpyrimidine-6-iminothiocarbonate,

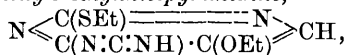
is prepared by the action of ethyl bromide and sodium on ethyl

5-ethoxy-2-ethylthiopyrimidine-6-thiocarbamate in alcoholic solution; it is obtained as an oil which reacts with ammonia in alcoholic solution, forming 6- ψ -ethylcarbamido-5-ethoxy-2-ethylthiopyrimidine,



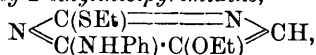
this crystallises from light petroleum, melts at 77° , and is converted slowly by concentrated hydrochloric acid into 6-carbamido-5-ethoxy-2-ethylthiopyrimidine, $\text{OEt} \cdot \text{C}_4\text{N}_2\text{H}(\text{SEt}) \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, which forms prismatic crystals and melts and decomposes at 166 — 167° .

6-Cyanamino-5-ethoxy-2-ethylthiopyrimidine,

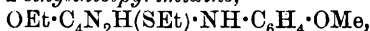


prepared by boiling 6- ψ -ethylcarbamido-5-ethoxy-2-ethylthiopyrimidine with sodium in benzene solution for forty hours, crystallises in white prisms, melts and effervesces slightly at 167 — 168° , is soluble in aqueous alkali hydroxides, is reprecipitated by acids, and is decomposed slowly by boiling water. The hydrochloride forms slender prisms and melts and decomposes at 175 — 180° .

6-Anilino-5-ethoxy-2-ethylthiopyrimidine,



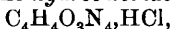
formed by boiling 6-chloro-5-ethoxy-2-ethylthiopyrimidine with aniline in alcoholic solution, crystallises from light petroleum in large prisms and melts at 60° . 6-p-Toluidino-5-ethoxy-2-ethylthiopyrimidine crystallises in long prisms, melts at 72° , and yields a hydrochloride, $\text{C}_{15}\text{H}_{19}\text{ON}_3\text{S} \cdot \text{HCl}$, which forms hair-like crystals and melts and decomposes at 105 — 106° . 6-o-Toluidino-5-ethoxy-2-ethylthiopyrimidine, $\text{C}_{15}\text{H}_{19}\text{ON}_3\text{S}$, crystallises from alcohol in flat prisms and melts at 80° ; the hydrochloride, $\text{C}_{15}\text{H}_{19}\text{ON}_3\text{S} \cdot \text{HCl}$, forms prisms and decomposes at 140 — 145° , or when dissolved in water. 6-p-Anisidino-5-ethoxy-2-ethylthiopyrimidine,



crystallises from alcohol in stout prisms and melts at 68 — 69° ; the hydrochloride, $\text{C}_{15}\text{H}_{19}\text{O}_2\text{N}_3\text{S} \cdot \text{HCl}$, forms prismatic crystals. 6-m-Nitroanilino-5-ethoxy-2-ethylthiopyrimidine, $\text{C}_{14}\text{H}_{16}\text{O}_3\text{N}_4\text{S}$, crystallises in long needles and melts at 125° ; the hydrochloride melts and decomposes at 125 — 135° .

G. Y.

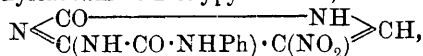
Pyrimidines: 5 Nitrocytosine and its Reduction to 5:6-Diamino-2-oxypyrimidine. XVII. TREAT B. JOHNSON, CARL O. JOHNS, and FREDERICK W. HEYL (*Amer. Chem. J.*, 1906, **36**, 160—177).—Nitrocytosine (Wheeler and Johnson, *Abstr.*, 1904, i, 624), which is formed in an 83.5 per cent. yield by the action of nitric acid of sp. gr. 1.5 on 6-amino-2-ethylthiopyrimidine, is 5-nitro-6-amino-2-oxypyrimidine, $\text{N} \begin{array}{c} \text{CO} \\ \text{C}(\text{NH}_2) \cdot \text{C}(\text{NO}_2) \end{array} \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} \text{NH} \rangle \text{CH}$, as (1) it yields nitouracil when heated with 20 per cent. sulphuric acid in a sealed tube at 185 — 197° , or when heated with nitrosyl chloride in aqueous hydrochloric acid solution in a sealed tube at 85 — 95° , and (2) it does not react with bromine. The hydrochloride of 5-nitrocytosine,



forms clusters of prisms and does not decompose below 300° .

The action of nitric acid of sp. gr. 1.5 on 5-bromo-6-amino-2-ethylthiopyrimidine leads to the formation of 5-bromocytosine.

5-Nitro-6-phenylcarbamido-2-oxypyrimidine,

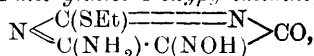


formed by heating 5-nitrocytosine with phenylthiocarbimide at 100°, decomposes, but does not melt, above 215°, and is insoluble in all solvents.

When boiled with acetic anhydride, 5-nitrocytosine yields mixtures of the *mono-* and *di-acetyl* derivatives; the latter, $\text{C}_8\text{H}_8\text{O}_5\text{N}_4$, forms needle-like prisms and decomposes at 273—275°.

5 : 6-Diamino-2-oxypyrimidine, $\text{N} \begin{array}{c} \text{CO} \\ \text{C}(\text{NH}_2) \cdot \text{C}(\text{NH}_2) \end{array} \begin{array}{c} \text{NH} \\ \text{CH} \end{array} \cdot \text{H}_2\text{O}$, is prepared by reduction of 5-nitrocytosine with aluminium amalgam and water below 35°; it forms clusters of prisms, loses H_2O at 120—130°, decomposes above 230°, forms an insoluble, red precipitate with potassium bismuth iodide, reduces platinum, gold, silver, and Fehling's solutions, has an alkaline reaction to litmus, and is precipitated by phosphotungstic acid. The *picrate*, $\text{C}_4\text{H}_8\text{ON}_4 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, forms spherical aggregates of prisms, commences to become brown at about 170°, and decomposes when more highly heated; the *mercurichloride*, $\text{C}_4\text{H}_6\text{ON}_4 \cdot \text{HgCl}_2$, was analysed.

6-Amino-5-nitroso-2-methylthiol-4-oxypyrimidine,



prepared by the action of sodium nitrite and glacial acetic acid on 6-amino-2-methylthiol-4-oxypyrimidine in aqueous sodium hydroxide solution, is reduced by ammonium sulphide to 5 : 6-diamino-2-methylthiol-4-oxypyrimidine, $\text{N} \begin{array}{c} \text{C}(\text{SEt}) \\ \text{C}(\text{NH}_2) \cdot \text{C}(\text{NH}_2) \end{array} \begin{array}{c} \text{NH} \\ \text{CO} \end{array}$, which crystallises in needles or prisms, melts and decomposes at 215—216°, is readily soluble in alcohol, and becomes red when exposed to air.

6-*p*-Toluidino-2-ethylthiolpyrimidine, $\text{N} \begin{array}{c} \text{C}(\text{SEt}) \\ \text{C}(\text{NH} \cdot \text{C}_7\text{H}_7) \end{array} \begin{array}{c} \text{N} \\ \text{CH} \end{array} \text{CH}$,

prepared by heating 6-chloro-2-ethylthiolpyrimidine with *p*-toluidine in benzene solution, crystallises in prisms, melts at 104°, and is readily soluble in alcohol or benzene; the *hydrochloride*, $\text{C}_{13}\text{H}_{15}\text{N}_3\text{S} \cdot \text{HCl}$, crystallises in needles and decomposes at 198—207°. When boiled with hydrochloric acid, the base yields 6-*p*-toluidino-2-oxypyrimidine, $\text{N} \begin{array}{c} \text{C} \\ \text{C}(\text{NH} \cdot \text{C}_7\text{H}_7) \cdot \text{CH} \end{array} \begin{array}{c} \text{NH} \\ \text{CH} \end{array}$, which melts and decomposes at 288—289°; the *hydrochloride*, $\text{C}_{11}\text{H}_{11}\text{ON}_3 \cdot \text{HCl}$, forms microscopic prisms and decomposes at 180—190°.

6-*o*-Toluidino-2-ethylthiolpyrimidine, $\text{N} \begin{array}{c} \text{C}(\text{SEt}) \\ \text{C}(\text{NH} \cdot \text{C}_7\text{H}_7) \end{array} \begin{array}{c} \text{N} \\ \text{CH} \end{array} \text{CH}$,

prepared from 6-chloro-2-ethylthiolpyrimidine and *o*-toluidine, crystallises from alcohol in prisms and melts at 87°; the *hydrochloride* $\text{C}_{13}\text{H}_{15}\text{N}_3\text{S} \cdot \text{HCl}$, forms granular crystals and melts and decomposes at 230—232°. When boiled with hydrochloric acid, the base forms

6-*o*-toluidino-2-oxypyrimidine, $\text{N} \begin{array}{c} \text{CO} \\ \text{C}(\text{NH} \cdot \text{C}_7\text{H}_7) \cdot \text{CH} \end{array} \begin{array}{c} \text{NH} \\ \text{CH} \end{array}$, which

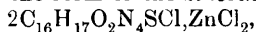
crystallises in stellate clusters of prisms and decomposes at 262° ; the *hydrochloride*, $C_{11}H_{11}ON_3 \cdot HCl$, forms lenticular crystals and decomposes at $227-231^{\circ}$.

6-*p*-Anisidino-2-ethylthiopyrimidine, $SEt \cdot C_4N_2H_2 \cdot NH \cdot C_6H_4 \cdot OMe$, is obtained as an oil; the *hydrochloride*, $C_{13}H_{15}N_3S \cdot HCl$, crystallises in needles and melts and decomposes at $200-201^{\circ}$. 6-*p*-Anisidino-2-oxypyrimidine, $C_{11}H_{11}O_2N_3$, melts at 262° ; the *hydrochloride*, $C_{11}H_{11}O_2N_3 \cdot HCl$, decomposes at $145-165^{\circ}$.

6-*m*-Nitro-2-ethylthiopyrimidine, $SEt \cdot C_4N_2H_2 \cdot NH \cdot C_6H_4 \cdot NO_2$, melts at 175° ; the *hydrochloride*, $C_{12}H_{12}O_2N_4S \cdot HCl$, forms needles and decomposes at $140-155^{\circ}$. 6-*m*-Nitro-2-oxypyrimidine, $C_{10}H_8O_3N_4$, is formed by boiling the preceding compound with hydrobromic acid; it crystallises in needle-like prisms and decomposes above 275° .

G. Y.

Methylene-green. EUGÈNE GRANDMOUGIN and E. WALDER (*Zeit. Farb. Ind.*, 1906, 5, 285-286).—The view that methylene-green is nitromethylene-blue (Gnehm and Walder, this vol., i, 390) is confirmed by the fact that it can be prepared by nitrating methylene-blue dissolved in 40 per cent. acetic acid with 50 per cent. nitric acid. The dye is separated in the form of the *zincchloride*,



which forms a dark brownish-violet, non-crystalline powder. The *hydriodide*, $C_{16}H_{16}O_2N_4S \cdot HI \cdot H_2O$, forms long, violet needles and crystallises well from water.

W. A. D.

Aromatic Azocyanamides. PAUL PIERRON (*Compt. rend.*, 1906, 143, 340-344).—*Benzeneazo-p-cyananilide*, $Ph \cdot N_2 \cdot C_6H_4 \cdot NH \cdot CN$, prepared by the action of diazobenzene chloride on the sodium derivative of cyananilide according to the equation $Ph \cdot N_2 \cdot Cl + NHPh \cdot CN = Ph \cdot N_2 \cdot C_6H_4 \cdot NH \cdot CN + NaCl$, or by the action of an alcoholic solution of cyanogen chloride or bromide on *p*-aminoazobenzene in the presence of alkali hydrogen carbonates, forms yellow, flattened needles melts at 163° , is readily soluble in alcohol, slightly so in benzene or ether, and almost insoluble in water; its alkaline solutions dye wool, silk, or mordanted cotton light yellow; it is hydrolysed by dilute acids, yielding the corresponding carbamide, *benzeneazo-p-phenylcarbamide*, $Ph \cdot N_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot NH_2$, which crystallises from alcohol in brownish-yellow needles, melts at 231° , is insoluble in water, slightly soluble in ether, chloroform, or benzene, more so in alcohol. The *benzoyl* derivative, $Ph \cdot N_2 \cdot C_6H_4 \cdot NBz \cdot CN$, forms short, hard, orange prisms, melts at 161° , is soluble in alcohol, and slightly so in benzene. *Benzeneazo-p-cyananilide* is reduced by stannous chloride, yielding aniline and *p*-aminophenylcarbamide, and reacts with hydroxylamine to form *p*-aminoazobenzene and phenylcarbamide.

Benzeneazo-p-cyano-o-toluidide, $Ph \cdot N_2 \cdot C_6H_3Me \cdot NH \cdot CN$, prepared similarly to the above compound, which it closely resembles, melts at 159° ; the *carbamide* and *benzoyl* derivatives melt at 207° and 141° respectively.

Benzeneazo-p-cyano-m-toluidide, $\text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}\cdot\text{CN}$, forms light yellow, pliable, silky needles, and melts at $118-119^\circ$ when gently or at 105° when rapidly heated; the *carbamide* and *benzoyl* derivatives melt at 152° and 134° respectively, and form long, flexible needles, the former dull reddish-yellow, the latter brilliant orange. *Benzeneazo- α -cyanonaphthylamide*, $\text{Ph}\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}\cdot\text{CN}$, forms a violet-red powder with a green reflex, melts indefinitely at $176-180^\circ$, and is very hygroscopic; the *carbamide* derivative melts at 253° .

Benzeneazo-o-ethoxy-p-cyanoanilide, $\text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{OEt})\cdot\text{NH}\cdot\text{CN}$, melts at 121° and crystallises from a mixture of light petroleum and benzene in orange-yellow needles; the *carbamide* derivative forms light yellow needles and melts at 206° .

p-Cyanotoluidide forms an unstable compound, probably the diazo-cyanamide, $\text{Ph}\cdot\text{N}_2\cdot\text{N}(\text{CN})\cdot\text{C}_6\text{H}_4\text{Me}$, with diazobenzene chloride, which rapidly decomposes, yielding a tarry, black mass containing the original cyanamide, the corresponding carbamide, and *p*-hydroxyazobenzene. The following equations indicate the probable course of the reactions: $\text{Ph}\cdot\text{N}_2\cdot\text{N}(\text{CN})\cdot\text{C}_6\text{H}_4\text{Me} + \text{H}_2\text{O} = \text{PhOH} + \text{N}_2 + \text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CN}$; $\text{Ph}\cdot\text{N}_2\cdot\text{N}(\text{CN})\cdot\text{C}_6\text{H}_4\text{Me} + \text{PhOH} = \text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH} + \text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CN}$.
M. A. W.

Salts of Benzeneazophenyltrimethylammonium. DANIEL VORLÄNDER, A. LOGOTHETIS, and A. J. PEROLD (*Annalen*, 1906, 345, 303-314).—The iodide, prepared from methyl iodide and dimethylaminoazobenzene, separates from water at 80° in orange-yellow crystals which melt at 184° , and from methyl or amyl alcohol in brown or orange-red crystals which melt at 173° .

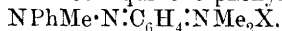
The iodide, precipitated by potassium iodide from a solution of benzeneazophenyltrimethylammonium chloride, melts at 178° , and after crystallisation from alcohol at 175° . By crystallisation from water, the melting point of the former substance rises to 183° , whereas that of the latter, after repeated crystallisation from alcohol, falls to $170-173^\circ$.

The *bromide*, prepared by shaking the iodide and silver bromide in water or alcohol, separates from water at 80° in crystals which melt at 196° , and from alcohol in leaflets melting at 192° . The leaflets occur in three forms. All these crystals, according to crystallographic measurements, belong to the same, probably to the rhombic, system.

The chloride, obtained from the iodide and silver chloride, separates from water in orange prisms, melts at 194° , and contains 1-2 mols. H_2O . The *zinc* salt, $(\text{C}_{15}\text{H}_{18}\text{N}_3\text{Cl})_2\cdot\text{ZnCl}_2$, separates from water in orange-yellow plates, melts at 201° , and contains $2\text{H}_2\text{O}$. The *platinichloride*, $(\text{C}_{15}\text{H}_{18}\text{N}_3)_2\text{PtCl}_6$, forms orange-yellow needles and melts and decomposes at $195-198^\circ$. The *nitrate* melts at 216° . The *picrate* forms yellow needles. The *carbonate* is obtained by evaporating in a vacuum a solution of the hydroxide saturated with carbon dioxide; it forms orange-red plates. The aqueous solution of the free base has a deep orange colour and an alkaline reaction; when freshly prepared it is odourless, but after some time acquires the odour of trimethylamine. By boiling

or by evaporation in a vacuum at 30—35° the solution decomposes and yields methylated amines, ammonia, dimethylaniline, *p*-dimethylaminoazobenzene, and a substance which melts at 126—127° and is sparingly soluble in hot water.

Aniline and not methylaniline results by the reduction of benzeneazophenyltrimethylammonium chloride by stannous chloride and hydrochloric acid; the chloride is therefore an ammonium-azo-compound, $\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{X}$, and not a quinone phenylhydrazone,



C. S.

Isomerism among the Hydroxyazo-compounds: 5-Azoisoeugenols. ERNESTO PUXEDDU (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 128—136).—The azo-derivatives of isoeugenol, like those of eugenol (Oddo and Puxeddu, *Abstr.*, 1905, i, 492), have the azo-group in the 5-position, taking the position of the propenyl group as 1. The change in the nature of the C_3H_5 substituent from allyl in the eugenol compounds to propenyl in the isoeugenol derivatives is accompanied by considerable changes in the physical and chemical characters. Thus, the azoisoeugenols cannot be obtained in a crystalline condition from alcohol or other solvents. They dissolve in dilute alkali hydroxide solutions, but do not separate out, as do the azoeugenols, without the addition of carbon dioxide or a mineral acid. When heated, they decompose without showing any definite melting point. They are not reduced by phenylhydrazine. On boiling with acetic anhydride and fused sodium acetate, they yield amorphous acetyl derivatives, which, when separated by the addition of water, emit an agreeable aromatic odour resembling that of raspberries.

Benzeneazoisoeugenol (compare Borsche and Streithberger, *Abstr.*, 1904, i, 1064) is obtained as a brick-red, amorphous powder, which dissolves in concentrated sulphuric acid, giving an intense brown coloration, and ignites on contact with fuming nitric acid. Its ethereal solution, on adding ethereal ferric chloride solution, assumes a brown colour.

o-Tolueneazoisoeugenol, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_2\cdot\text{C}(\text{OH})\cdot\text{C}(\text{OMe})\cdot\text{CH}=\text{C}(\text{CHMe})\cdot\text{CH}(\text{CHMe})$, is a reddish-brown powder, readily soluble in the ordinary organic solvents, excepting light petroleum and carbon tetrachloride, in which it dissolves only sparingly. It begins to darken and decompose at 62°.

m-Tolueneazoisoeugenol, $\text{C}_{17}\text{H}_{18}\text{O}_2\text{N}_2$, forms a red powder which begins to decompose at about 100°, and dissolves slightly in light petroleum or carbon tetrachloride and readily in other organic solvents. Concentrated sulphuric acid dissolves it, giving an intensely brown solution, and nitric acid causes it to ignite.

β -Naphthaleneazoisoeugenol, $\text{C}_{20}\text{H}_{18}\text{O}_2\text{N}_2$, is obtained as a brick-red powder, which dissolves readily in the more common organic solvents. α -Naphthaleneazoisoeugenol is an amorphous, reddish-brown powder, which decomposes without melting.

o-Nitrobenzeneazoisoeugenol is a reddish-brown powder which begins to decompose at about 120°, and dissolves readily in organic solvents. *p*-Nitrobenzeneazoisoeugenol was also prepared.

T. H. P.

Chemical Action of Light. ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 136—138).—On subjecting *s*-tribromodiazobenzene *syn*.-cyanide, in benzene solution, to the action of light for three days, it is completely transformed into the corresponding *anti*-compound (compare Hantzsch and Schultze, *Abstr.*, 1895, i, 348).

T. H. P.

Action of Dilute Hydrochloric Acid on Albumins. ED. SWIRLOWSKY (*Zeit. physiol. Chem.*, 1906, 48, 252—299. Compare Lawroff, *Abstr.*, 1905, ii, 178).—The prolonged action of 0.5 per cent. hydrochloric acid on the following proteids at 36—38° has been investigated, care being taken that putrefaction did not occur and that proteolytic enzymes were absent: gelatin, albumin from the blood serum of horses, casein, crystallised hæmoglobin from horse's blood, and albumoses obtained from Witt's peptone. The effects produced by the acid are similar to those observed during peptic digestion, but the reaction proceeds far more slowly. Monoamino-acids or combinations of such acids are formed; these are not precipitated by phosphotungstic acid and are decomposed by 20 per cent. hydrochloric or sulphuric acid into free amino-acids. The intensity of the action is different with the different proteids. Gelatin is least readily hydrolysed, so that at the end of 150 days the presence of free amino-acids cannot be demonstrated, as is the case with the other proteids. Previous drying of the proteids does not appear to affect the hydrolysis.

J. J. S.

The Nucleic Acid from the Spermatozoa of *Murænaeox cinereus*. KATSUJI INOUE (*Zeit. physiol. Chem.*, 1906, 48, 181—184. Compare this vol., i, 55).—A nucleic acid has been isolated from the mature spermatozoa of *Murænaeox cinereus* Forsk. It appears to contain slightly more nitrogen and phosphorus than the nucleic acid from the intestine. When hydrolysed with 20 per cent. sulphuric acid, it yields lævulic acid, guanine, adenine, xanthine, hypoxanthine, cytosine, and thymine.

J. J. S.

Preparation and Composition of Myco-nucleic Acids from Yeast. WILLIAM F. BOOS (*Chem. Centr.*, 1906, i, 1833; from *Arch. exp. Path. Pharm.*, 55, 16—20).—Nucleic acids prepared from yeast by the method adopted by Herlant (*Abstr.*, 1900, i, 466) exhibited variations in the amount of oxygen similar to those observed by Herlant. Four different preparations gave the compositions: (1) $C_{36}H_{52}O_{14}N_{14}(P_2O_5)_2 + 8O$, (2) $C_{36}H_{52}O_{14}N_{14}(P_2O_5)_2 + 3O$, (3) and (4) $C_{36}H_{52}O_{14}N_{14}(P_2O_5)_2 + 2H_2O$. With another method of preparation in which any possible variation in the action of the potassium was avoided, a nucleic acid of the composition $C_{36}H_{52}O_{14}N_{14}(P_2O_5)_2$ was obtained.

T. H. P.

Latschinoff's Cholocamphoric Acid. THEODOR PANZER (*Zeit. physiol. Chem.*, 1906, 48, 192—204. Compare Latschinoff, this Journal, 1880, 56, 722).—Cholocamphoric acid, obtained by the oxidation of cholic acid with nitric acid, crystallises from water in long, slender, silky needles and dissolves readily in glacial acetic acid

or in 80 per cent. alcohol. When quickly heated, it turns brown at 270° and decomposes at 286° . The analytical results agree best with the formula $C_{14}H_{22}O_6$, and not the formula $C_{10}H_{16}O_4$, suggested by Latschinoff. It appears to be a tribasic acid, but a crystalline anhydride has not been prepared. When the acid is distilled with lime, a benzene hydrocarbon, $C_{11}H_{16}$, distilling at 227° (uncorr.) is obtained. When the hydrocarbon is oxidised, benzoic and phthalic acids do not appear to be formed, and it is thus probable that in both the hydrocarbon and in the acid at least three side-chains are present. The hydrocarbon is a benzene derivative, and the acid a hexamethylene compound.

J. J. S.

Diamino-acids derived from Egg-albumin. LOUIS HUGOUNENQ and J. GALIMARD (*Compt. rend.*, 1906, 143, 242—243).—By hydrolysing egg-albumin with dilute sulphuric acid in presence of sodium chloride, the authors have obtained (1) 2.14 per cent. of arginine; (2) 2.15 per cent. of lysine; (3) a white compound, $C_{11}H_{18}O_4N_5$, which crystallises in small needles, soluble in water, but insoluble in alcohol, and is precipitated by acid mercuric sulphate solution; it appears to be a compound of arginine with an acid amide, such as pyrrolidine-2-carboxylic acid; (4) a compound which is not precipitated by mercuric sulphate and yields a hydrochloride, $C_{10}H_{19}O_6N_5 \cdot 2HCl$, crystallising in moderately hard, white prisms; this compound is probably a derivative of arginine and aspartic acid. Histidine is absent. T. H. P.

The True Nature of Lepierre's α -Glucoproteins. J. GALIMARD, L. LACOMME, and ALBERT MOREL (*Compt. rend.*, 1906, 143, 298—300).—The constitution ascribed by Lepierre (*Abstr.*, 1901, i, 622) to the nitrogenous compounds (glucoproteins) which he employed for the cultivation of micro-organisms is inexact; his so-called " α -glucoproteins" are mixtures of monoamino-acids (alanine, leucine, and phenylalanine) containing traces of tyrosine and non-crystalline substances (Hugounenq and Morel, this vol., i, 719), and it is these which play the most important part in the nutrition of the micro-organisms, for the nutritive value of the " α -glucoproteins" is destroyed when all traces of tyrosine and non-crystalline substances are removed by means of repeated crystallisations.

M. A. W.

Amount of Phosphorus in Egg-albumin. KARL KAAS (*Monatsh.*, 1906, 27, 403—409. Compare Hofmeister, *Abstr.*, 1898, i, 390; Hopkins and Pinkus, *ibid.*, 456).—The albumin of a fresh hen's egg contained 0.155 per cent., whilst that of an egg one month old contained 0.228 per cent., of phosphorus, the difference being probably in consequence of diffusion of phosphorus from the yolk. Crystalline egg-albumin prepared by Hofmeister and Hopkins's method and Pinkus's method contained 0.919 per cent., but after elimination of the amino-groups by treatment with sodium nitrite and glacial acetic acid, 2.42 per cent., of phosphorus. Of two specimens of pure

egg-albumin, the one prepared by Hofmann and Pinkus' method, and freed from ammonium sulphate by dialysis, contained 0.352 per cent. of phosphorus, whilst the other, prepared by Hammarsten's process, was free from phosphorus. G. Y.

Animal Gelatins. V. Preparation of Gelatins. WL. S. SADIKOFF (*Zeit. physiol. Chem.*, 1906, 48, 130—139. Compare Abstr., 1904, i, 125, 126, 462; this vol., i, 224).—The various methods for the preparation and purification of gelatin are discussed. Most of these methods are tedious, remove but part of the impurities, and produce a partial decomposition of the gelatin. The following method is recommended. Pounded bones are extracted with fresh amounts of hydrochloric acid (1:3) for seven to eight days, and then, after washing with water, transferred to a 1—3 per cent. solution of sodium hydroxide. By this method all albumins, mucin, nucleo-proteids, &c., are dissolved, any calcium phosphate is precipitated, and fatty compounds are hydrolysed. After the alkaline liquid has been changed three times, the residue is washed with water and the hyaline mass added to a boiling 1 per cent. solution of chloroacetic acid. The gelatin-yielding substances are readily transformed into gelatin, and after filtration the gelatin may be precipitated by the aid of magnesium sulphate and then washed with water and alcohol.

Gelatin prepared by the ordinary method may be purified by washing with water and then with a cold 20 per cent. aqueous solution of magnesium sulphate. It is then dissolved in warm 20 per cent. magnesium sulphate solution, filtered hot, and to the cold filtrate is added a 0.5 per cent. solution of hydrochloric or sulphuric acid in 20 per cent. magnesium sulphate. The precipitate is removed, washed, dissolved in hot water, and very dilute acid and much alcohol are added, and then the gelatin precipitated by neutralisation with ammonia. J. J. S.

Absorption of Gallic Acid by Organic Colloids. WILLIAM P. DREAPER and ALEXANDER WILSON (*J. Soc. Chem. Ind.*, 1906, 25, 515—518).—A detailed account of the experimental results, of which a summary has been published previously (*Proc.*, 1906, 22, 70).

P. H.

Kyrines. MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1906, 48, 54—68. Compare Abstr., 1903, i, 586; 1905, i, 104).—Kyrines, the intermediate decomposition products of proteids by acids, are characterised by the constancy of the composition of their sulphates, by the relationship of the nitrogen precipitated by phosphotungstic acid to the total nitrogen, and by their forming characteristic phosphotungstates. Skraup and Zwerger's doubts (this vol., i, 123) as to the homogeneity of caseinokyrine are investigated, and, by following the change in rotation, the hydrolysis of casein at 100° and at 38° is compared. It is possible when mixtures of kyrine sulphate and lysine are precipitated with phosphotungstic acid to distinguish microscopically the mixed phosphotungstates. The picrates also afford a means of distinguishing caseinokyrine from lysine and arginine, the former separating always

as an oil, whereas lysine picrate crystallises immediately the excess of picric acid is removed by ether.

Kyrine obtained from fibrin yields lysine, arginine, and glutamic acid on hydrolysis. Constancy in the composition of the sulphate was obtained after the ninth precipitation; 72.7 per cent. of the nitrogen was then in a form precipitable by phosphotungstic acid and about half the total was in the form of arginine.

E. F. A.

Hydrolysis of Meat Extract. KARL MICKO (*Zeit. Nahr. Genussm.*, 1906, 11, 705—729).—The constituents of the mixture obtained on hydrolysing meat extract were separated by Emil Fischer's ester method, alanine, leucine, glycine, and valeric acid being obtained in the earlier fractions. Considerable quantities of lactic acid and of succinic acid were also proved to be present. In all about 20 per cent. of the organic matter of the meat extract was regained in the form of amino-acids. Of these, glutamic acid was present in largest amount; besides those mentioned above, *isoleucine* and aspartic acid were also isolated. Similar products were obtained on directly esterifying the meat extract.

E. F. A.

Proteid Reactions attributed to Tryptophan. FRANZ BARDACHZI (*Zeit. physiol. Chem.*, 1906, 48, 145—159. Compare Hopkins and Cole, *Abstr.*, 1901, i, 310).—The coloured solutions obtained by treating tryptophan with "active" ether and dissolving in hydrochloric acid have been examined by means of a Hüfner spectrophotometer and the light extinction curves drawn. Different solutions give similar curves, but of varying intensity, the variations depending to a certain extent on the amount of ether used.

Solutions obtained by dissolving tryptophan in hydrochloric acid mixed with dilute glyoxylic acid have been examined similarly. When kept, these solutions become paler, but yield practically the same photometric curve. The effect of warming, however, is to force the extinction towards the blue end of the spectrum; but when a further quantity of glyoxylic acid is added to the cooled solution, the original colour and extinction are restored.

Solutions of tryptophan in hydrochloric acid and furfuraldehyde rapidly darken and cannot be examined in the same way.

Various proteids, such as ovalbumin, casein, &c., have been experimented with in the same manner as tryptophan; the clear, coloured solutions are usually obtained on warming only. The colorations are somewhat similar to those given by tryptophan, but the extinction curves are quite different.

The solutions obtained by dissolving cholic acid in fuming hydrochloric acid and furfuraldehyde and in hydrochloric acid and sucrose (2 per cent.) give curves which do not resemble one another.

J. J. S.

Photographic Determination of the Absorption Bands of the Colouring Matters of Blood. LOUIS LEWIN, A. MIETHE, and E. STENGER (*Compt. rend.*, 1906, 143, 115—117).—The absorption spectra of blood, of hæmoglobin, and of some of its derivatives have

been photographed and measured in terms of wave-lengths. From a large number of experiments with solutions of different concentrations, the most suitable dilution for the measurement of a particular band has been determined. The detailed results are summarised in a table. It appears that the absorption bands in the less refrangible part of the spectrum are in general less characteristic than those in the more refrangible portion.

H. M. D.

Formation of Methæmoglobin. I. ALLEXIS BABEL (*Arch. Sci. phys. nat.*, 1906, [iv], 22, 146—162).—The author has examined, spectroscopically, the action on pig's blood of a number of simple organic compounds, such as aniline and phenol and their principal derivatives, in order to determine their relative capacities for converting oxyhæmoglobin into methæmoglobin. Numbers are given expressing the minimum quantities in grams of the various substances required to produce an absorption band of a certain intensity when allowed to act for three hours at 20° on 20 c.c. of blood diluted to a concentration of about 5 per cent.

The methæmoglobinising activities of the substances examined are analogous to their chemical reactivities. All causes tending to render the molecule of a compound more stable, and so to diminish its capability of combination, exert influences in the same sense on the formation of methæmoglobin. Thus, the introduction of a sulphonic or carboxyl group into a molecule renders it much more resistant to the action of reagents; the sulphanilates and anthranilates have also much less marked hæmoglobinising actions than aniline, from which they are derived.

T. H. P.

Action of Sodium Fluoride on Methæmoglobins obtained from Globin and Hæmatin. JOSEPH MOITESSIER (*Bull. Soc. chim.*, 1906, [iii], 35, 575—576).—The author has investigated the optical effect produced by the addition of sodium fluoride to solutions of methæmoglobins synthesised from globin and hæmatin from various sources (Bertin Sans and Moitessier, *Abstr.*, 1894, i, 216), and finds that the absorption bands are intensified and displaced as recorded by Ville and Derrien (*Abstr.*, 1905, i, 399, 500).

T. A. H.

Colouring Matter of Blood. VI. JOZEF BURACZEWSKI and LEON MARCHLEWSKI (*Zeit. physiol. Chem.*, 1906, 47, 331—334. Compare *Abstr.*, 1905, i, 399).—The product obtained by distilling α -methyl- β -propylmaleimide with zinc dust in an atmosphere of hydrogen condenses with diazobenzene chloride, yielding an azo-dye, the optical properties of which resemble those of the hæmopyrrolebisazo-dye. But although the hydrochloride of the latter crystallises readily, the hydrochloride of the dye from the synthetical product has not been obtained so far in a crystalline form.

J. J. S.

Specific Action of Peroxydases. ROBERT CHODAT (*Ber.*, 1906, 39, 2506—2507).—A claim for priority on behalf of Chodat and Bach as against Bach (this vol., i, 616).

G. Y.

Hydrolytic Activity of Liver Histozyms and Enzymes on some Glucosides and Alkaloids. MAX GONNERMANN (*Pflüger's Archiv*, 1906, 113, 168—197).—The action of the extract of the liver of the ox, hare, dog, horse, and fish, and a number of enzymes also of some bacilli has been investigated, using the glucosides sinigrin, arbutin, amygdalin, sapotoxin, and the alkaloids atropine, cocaine, morphine, and hydroxydimorphine as test materials. In no instance is sinigrin affected, showing the rarity of the occurrence of myrosin. Arbutin is hydrolysed by the liver extracts, by emulsin, by some bacilli, and by tyrosinase. Amygdalin is affected by the liver extracts of the ox and hare alone, also by trypsin, emulsin, and some bacilli, whilst it is hydrolysed within twenty-four hours by tyrosinase. Sapotoxin is hydrolysed by liver extracts and also by emulsin and tyrosinase. Atropine is attacked by the liver enzymes, also by pancreatin, by trypsin, and by tyrosinase. Cocaine by the histozyms, by pancreatin, trypsin, and emulsin, and by bacilli, but not by pepsin, maltase, or invertase. Morphine is only positively attacked by tyrosinase, and partially, perhaps, by the liver histozyms of the hare and the dog. All the enzymes were without action on hydroxydimorphine.

E. F. A.

Effect of Heat on Enzyme Activity. WILHELM CRAMER and A. R. BEARN (*Proc. Physiol. Soc.*, 1906, xxxvi—xxxvii; *J. Physiol.*, 34).—Experiments with pepsin and rennin show that the presence of the enzyme inactivated by heating to 56—60° hinders, or in sufficient amount completely inhibits, the action of the active enzyme. Heating to 100° weakens or destroys their power. If enzyme action consists of the stages (1) the formation of a compound between substrate and enzyme, and (2) the breaking down of this compound, then the above results are explicable as follows: heating to 60° has not affected the first stage; the substrate which has combined with the inactivated enzyme cannot therefore take up the active enzyme, and is thus protected from its action. Heating to 100° changes the structure of the enzyme so profoundly that it can no longer combine with the substrate.

W. D. H.

Enzymes in Relation to Concentrated Electric Light. SIGVAL SCHMIDT-NIELSEN (*Beitr. chem. Physiol. Path.*, 1906, 8, 481—483. Compare Abstr., 1905, ii, 48).—Concentrated electric light inactivates chymosin (rennin) to a very considerable extent. The same is true for its zymogen and for the anti-rennin of blood-serum.

W. D. H.

Organic Chemistry.

Acetyl Chloride and Hydrochloric Acid as Reagents for distinguishing between the Various Types of Monohydric Alcohols. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1906, 261—280).—Acetyl chloride reacts with primary or secondary alcohols, converting them quantitatively into esters of acetic acid (with evolution of hydrogen chloride), whereas tertiary alcohols under the same conditions are converted into chlorides.

These two reactions were found to take place concurrently and independently of each other when mixtures of tertiary with primary or secondary alcohols were treated with acetyl chloride.

Tertiary alcohols, except those of very high molecular weight, dissolve at once in fuming hydrochloric acid; the solution rapidly becomes turbid owing to the formation of the chloride, which rises to the surface as an oil. This change takes place in the cold, although the reaction is facilitated by warming gently. Primary or secondary alcohols, on the other hand, also dissolve in fuming hydrochloric acid, and two layers are again formed after a time, but the upper one in this case consists only of the unchanged alcohol saturated with hydrogen chloride, no esterification taking place unless the mixture is warmed.

P. H.

Application of the Principle of Partition. VI. Action of Hydrogen chloride on Propylene Oxide and Propenyl Alcohol. ARTHUR MICHAEL (*Ber.*, 1906, 39, 2785—2789. Compare this vol., i, 620).—By the action of dry hydrogen chloride in the cold on propylene oxide, a chlorohydrin is formed, which boils at 127—127·5° (corr.) under 722 mm. pressure and has a sp. gr. 1·113 at 20°/20°; allyl chloride yields a chlorohydrin, boiling at 126—126·5° (corr.) under 722 mm. pressure, and having a sp. gr. 1·115 at 20°/20°. The compound is probably therefore ω -chloroisopropyl alcohol, $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$, containing a small quantity of β -chloropropyl alcohol. The chlorohydrin from propenyl alcohol boiled at 127—127·5°, and had a sp. gr. 1·112 at 20°/20°; it also consisted mainly of ω -chloroisopropyl alcohol.

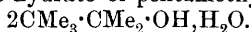
E. F. A.

Application of the Principle of Partition. VII. Action of Hydrogen Chloride on *iso*Butylene Oxide. ARTHUR MICHAEL and VIRGIL L. LEIGHTON (*Ber.*, 1906, 39, 2789—2795. Compare preceding abstract).—By the action of dry hydrogen chloride on *isobutylene* oxide, an *isobutylene* chlorohydrin is obtained, which boils at 127—130°, and has a sp. gr. 1·0587 at 20°/20°, whereas the product $\text{CH}_3\text{Cl}\cdot\text{CMe}_2\cdot\text{OH}$, obtained by the addition of hypochlorous acid to *isobutylene*, boils at 128—129° and has a sp. gr. 1·0663 at 20°/20°. The *isobutylene* chlorohydrin when warmed with aqueous sodium carbonate or potassium acetate forms *isobutaldehyde*, and behaves, in fact, as if it were a mixture of one

part of $\text{CMe}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ and two parts of $\text{CH}_2\text{Cl}\cdot\text{CMe}_2\cdot\text{OH}$, a supposition confirmed by decomposition with phosphoric oxide, when a mixture of isomeric chloroisobutylenes is obtained two-thirds as great as if obtained from β -chloroisobutyl alcohol.

E. F. A.

New Syntheses of Pentamethylethanol and of Hexamethylethane. LOUIS HENRY [with AUG. DE WAELE] (*Bull. Acad. roy. Belg.*, 1906, 352—363. Compare this vol., i, 477).—Pentamethylethanol may be prepared either by the action of magnesium methyl bromide on pinacolin or by the action of acetone on *tert.*-butyl chloride and magnesium. Hexamethylethane is obtained by acting on magnesium methyl bromide with an ethereal solution of bromopentamethylethane; the latter substance was prepared by passing hydrogen bromide into an alcoholic solution of the hydrate of pentamethylethanol,

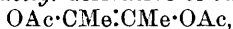


Bromopentamethylethane, $\text{CMe}_3\cdot\text{CMe}_2\text{Br}$, is a white solid which gradually becomes faintly yellow; it melts and partially decomposes in a sealed capillary tube at 143° . When heated in an open tube it volatilises; the substance has an odour of camphor, is very slightly soluble in alcohol, but dissolves readily in ether.

P. H.

Action of Sodium on Esters of Fatty Acids. Preparation of Acyloins of the Type $\text{R}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{R}$. Mechanism of the Reaction. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1906, [iii], 35, 629—633, 633—636).—The first paper gives a general account of work already dealt with in Abstr., 1903, i, 597, 673, 730; 1904, i, 213, 642; 1905, i, 11, 12, 13, 560, and suggests the general name "acyloins" for the hydroxyketones of the type $\text{R}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{R}$ produced in this reaction.

The yellow sodium derivative, eventually precipitated when ethyl acetate is treated with sodium by the general method already described (Abstr., 1905, i, 560), is converted by acetyl chloride into acetyl-methylcarbinyl acetate, $\text{COMe}\cdot\text{CHMe}\cdot\text{OAc}$ (van Reymenant, Abstr., 1901, i, 126), and the *diacetyl* derivative of *butene-2:3-diol*,



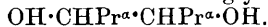
which has a sp. gr. 0.950 at $0^\circ/4^\circ$ and boils at 110 — 115° under 29 mm. pressure. The former is produced by partial hydrolysis of the latter. From these reactions it appears that the yellow sodium derivative must have the constitution $\text{ONa}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{ONa}$, and that the formation of acyloins from esters takes place in the following steps: $2(\text{R}\cdot\text{CO}_2\text{Et}) \rightarrow \text{ONa}\cdot\text{CR}\cdot\text{CR}\cdot\text{ONa} \rightarrow \text{OH}\cdot\text{CR}\cdot\text{CR}\cdot\text{OH} \rightarrow \text{R}\cdot\text{CO}\cdot\text{CHR}\cdot\text{OH}$.

T. A. H.

Acyloins of the Fatty Series. III and IV. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1906, [iii], 35, 637—641, 641—643. Compare Abstr., 1905, i, 560, 572, and preceding abstract).—Propioin, $\text{COEt}\cdot\text{CHEt}\cdot\text{OH}$, boils at 72 — 73° under 20 mm. pressure, has sp. gr. 0.968 at $0^\circ/4^\circ$, and polymerises slightly when distilled at atmospheric pressure (compare Anderlini, Abstr., 1896, i, 202). The *acetyl* derivative has a sp. gr. 1.001 at $0^\circ/4^\circ$ and boils at 85 — 96° under

17 mm. pressure. The *semicarbazone* forms small crystals, melts at 137° , and is readily soluble in water.

Butyroin, $\text{COPr}^{\alpha}\cdot\text{CHPr}^{\alpha}\cdot\text{OH}$, boils at 85° under 10 mm. pressure (compare Klinger and Schmitz, Abstr., 1891, 890). Its oxime (Abstr., 1905, i, 572, and Münchmeyer, Abstr., 1886, 350), when heated with acetic anhydride, decomposes into butyraldehyde and propyl cyanide. The *acetyl* derivative has a sp. gr. 0.9807 at $0^{\circ}/4^{\circ}$ and boils at $117\text{--}118^{\circ}$ under 21 mm. pressure. When butyroin is heated with potassium hydroxide in water, the principal product is a mixture of the two stereoisomeric modifications of the glycol,



The dipropylglycollic acid which Klinger and Schmitz obtained from their butyroin in this reaction was probably formed by the action of the alkali on some dibutyryl present in the butyroin used. A mixture of butyroin and pyruvic acid when heated yields butyroin pyruvate and a liquid having the properties of 4-octanone. The former forms with semicarbazide a substance having the composition of a semicarbazone, less 1 mol. of water (compare Abstr., 1905, i, 572). Butyroin on heating with sulphuric acid yields *dibutyroin*, $\text{C}_{16}\text{H}_{28}\text{O}_2$, which is liquid, has sp. gr. 0.939, and boils at $155\text{--}157^{\circ}$ under 12 mm. pressure.

*iso*Butyroin, $\text{COPr}^{\beta}\cdot\text{CHPr}^{\beta}\cdot\text{OH}$, has sp. gr. 0.931 and boils at 83° under 26 mm. pressure (compare Klinger and Basse, *loc. cit.*). The *oxime* melts at $110\text{--}111^{\circ}$ and boils at 137° under 14 mm. pressure; a semicarbazone could not be obtained.

Hexonoin, $\text{C}_5\text{H}_{11}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{C}_5\text{H}_{11}$, has a sp. gr. 0.910 at $0^{\circ}/4^{\circ}$, boils at $130\text{--}132^{\circ}$ under 8 mm. pressure, and when dehydrated by sulphuric acid yields dihexonoin, which boils at $225\text{--}230^{\circ}$ under 10 mm. pressure (compare Abstr., 1905, i, 561, 573).

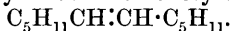
Pivaloin, $\text{CMe}_3\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CMe}_3$, prepared by the general method from methyl pivalate, crystallises from ether in small needles, melts and sublimes at 81° , and is very stable. Like *isobutyroin* it does not yield a semicarbazone.

T. A. H.

Hydrogenation of Fatty Acyloins. Preparation of *s*-Dissecondary Glycols, Alcohols of the Type $\text{OH}\cdot\text{CHR}\cdot\text{CH}_2\text{R}$, and the Corresponding Ketones. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1906, [iii], 35, 643—646, 646—650. Compare preceding abstracts).—The reduction is effected by allowing an alcoholic solution of the acyloin to drop slowly into a flask containing large fragments of sodium. The products of the action are (1) a mixture of the two stereoisomeric modifications of the symmetric dissecondary glycol of the type $\text{OH}\cdot\text{CHR}\cdot\text{CHR}\cdot\text{OH}$, and (2) a secondary alcohol of the type $\text{CH}_2\text{R}\cdot\text{CHR}\cdot\text{OH}$, the former being always produced in the larger quantity. Since both these reduction products are readily convertible into ketones of the type $\text{RCO}\cdot\text{CH}_2\text{R}$, the former by heating with dilute sulphuric acid at 180° in closed vessels and the latter by oxidation with chromic acid, these reactions furnish a means of converting acyloins almost quantitatively into these ketones, which the authors suggest might be called homoacylones, the symmetrical ketones, $\text{R}\cdot\text{CO}\cdot\text{R}$, being known as acylones. The products obtained from

butyroin and hexonoin by these reactions are described in Abstr., 1905, i, 573.

When the mixture of the two stereoisomeric dodecane- $\xi\eta$ -diols are treated with phosphorus chloride or bromide, they furnish the two corresponding stereoisomeric halogen derivatives. The mixture of dichloro-derivatives boils at 115—135° under 10 mm. pressure and is scarcely affected by zinc dust in presence of alcohol, but the mixture of the dibromo-derivatives, similarly obtained, which boils at 145° under 10 mm. pressure, is readily reduced to dodecylene,



The purest specimen of this obtained contained from 25 to 30 per cent. of a saturated hydrocarbon and boiled at 208—209°. T. A. H.

"Steric Hindrance" in Derivatives of Pivaloin. LOUIS BOUEVAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1906, [iii], 35, 655—657).—Whilst the normal acyloins condense readily with semicarbazide, *isobutyroin* does so only with difficulty (this vol., i, 783). Further, whilst hydroxylamine readily gives dioximes with the normal α -diketones, it reacts much less readily with *diisobutyryl*. These observations indicate that the reactivity of a carbonyl group is lessened by the multiplication of methyl groups in its vicinity. This influence is at its maximum in *pivaloin*, $\text{CMe}_3\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{CMe}_3$, which does not form a semicarbazone (this vol., i, 783). Further, on reduction with sodium and alcohol it does not yield the corresponding glycol, but only the *monohydric alcohol*, $\text{CMe}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CMe}_3$, which separates from light petroleum in splendid crystals, melts at 52—53°, boils at 173—174°, sublimes readily, and is volatile in a current of steam. On oxidation with chromic acid in presence of sulphuric acid, it yields *homopivalone*, $\text{CMe}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CMe}_3$, an unpleasant-smelling liquid, which has a sp. gr. 0.827 at 0°/4° and boils at 163°. Even when heated with hydroxylamine hydrochloride and zinc oxide for seven hours, this ketone furnishes no oxime and similarly it yields no semicarbazone.

Dipivaloyl, $\text{CMe}_3\cdot\text{CO}\cdot\text{CO}\cdot\text{CMe}_3$, obtained by dehydrogenating *pivaloin* by Sabatier and Senderens' method, is a yellow liquid, has sp. gr. 0.895 at 0°/4°, and boils at 70° under 21 mm. and at 169—170° under atmospheric pressure. When heated with hydroxylamine hydrochloride and zinc oxide in great excess for twenty-four hours, it yields about 30 per cent. of the *monoxime*, which separates from light petroleum in slender needles and melts at 123°. T. A. H.

tert.-**Pinacolyl Alcohol.** MAURICE DELACRE (*Bull. Acad. roy. Belg.*, 1906, 281—287).—The alcohol obtained by the action of acetone on *isopropyl bromide* and magnesium boils at 118.8—119.6° and still remains liquid at -15°, whereas the substance obtained by the reduction of *pinacolin* boils at 120.2—120.6° and melts at +3.6°; the synthetic compound is also more mobile. P. H.

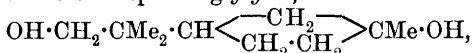
Preparation of γ -, δ -, ϵ -, &c., Glycols and their Derivatives from the Corresponding Lactones. FRIEDRICH W. SEMMLER (*Ber.*, 1906, 39, 2851—2857).—Good yields of γ -, δ -, &c., glycols are

readily obtained by reducing the corresponding lactones with sodium and boiling alcohol. The following glycols have been prepared by this method. Pentane- $\alpha\delta$ -diol from γ -valerolactone; a by-product is hydroxyvaleric acid. A glycol, $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}(\text{CH}_2\cdot\text{OH})\\ \text{CH}_2\text{---CH}_2\end{smallmatrix}\right\rangle\text{CHMe}$ or

$\text{OH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}(\text{CH}_2\cdot\text{OH})\\ \text{CH}_2\text{---CH}_2\end{smallmatrix}\right\rangle\text{CHMe}$, from the lactone of pulegic acid; it distils at $137\text{--}140^\circ$ under 10 mm. pressure, and has n_D 1.4715 and a sp. gr. 0.9945 at 20° . With concentrated sulphuric acid, it yields an oxide, $\text{C}_{10}\text{H}_{18}\text{O}$. $\beta\zeta$ -Dimethyloctane- $\gamma\theta$ -diol, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CHMe}_2$, boiling at 147° under 10 mm. pressure, from the lactone of ϵ -hydroxy- $\beta\zeta$ -dimethyl-octoic acid (Baeyer, Abstr., 1900, i, 329).

α -Hydroxydihydrocinnamyl alcohol, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, a liquid distilling at $177\text{--}178^\circ$ under 8 mm. pressure and having a sp. gr. 1.1293 at 20° and n_D 1.55984, is prepared from coumarin. Its benzoyl derivative melts at $99\text{--}100^\circ$, and with sulphuric acid the alcohol gives a good yield of chroman (Abstr., 1905, i, 294).

The compound obtained by Czerny (Abstr., 1900, i, 675) by the action of concentrated sulphuric acid on α -fencholenic acid (Cockburn, Trans., 1899, 75, 506) is the lactone of α -fencholenic acid, and on reduction yields the corresponding glycol,



which boils at $158\text{--}161^\circ$ under 11 mm. pressure. With sulphuric acid, it yields an oxide, which is identical with Wallach's fenchol (Abstr., 1895, i, 381).

The lactone of β -fencholenic acid, $\text{C}_{10}\text{H}_{16}\text{O}_2$, boils at $116\text{--}118^\circ$ under 8 mm. pressure, has a sp. gr. 1.0343 at 25° , and when reduced yields the glycol, $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CH}_2\\ \text{---CH}_2\end{smallmatrix}\right\rangle\text{CMe}\cdot\text{CH}_2\cdot\text{OH}$, boiling at $142\text{--}143^\circ$ under 8—9 mm. pressure.

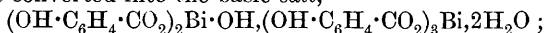
J. J. S.

Action of the Polyhydric Alcohols on Bismuth Salts and the Preparation of Bismuth Salts by means of a Solution of Mannitol Bismuth Nitrate. LUDWIG VANINO and F. HARTL (*J. pr. Chem.*, 1906, [ii], 74, 142—152. Compare Vanino and Hauser, Abstr., 1902, i, 8).—On addition of much acetone to an aqueous solution of mannitol bismuth nitrate, there is formed a hard crystalline compound, $2\text{Bi}(\text{NO}_3)_3\cdot\text{C}_6\text{H}_{14}\text{O}_6$, which is very soluble in water. Sorbitol and dulcitol behave towards bismuth nitrate in the same manner as does mannitol. The white, crystalline precipitate, $\text{Bi}(\text{NO}_3)_3\cdot\text{C}_6\text{H}_{14}\text{O}_6$, obtained on addition of acetone to the sorbitol bismuth nitrate solution, is readily soluble in water; the similar precipitate obtained from the dulcitol bismuth nitrate solution has the composition $\text{BiO}\cdot\text{NO}_3\cdot\text{C}_6\text{H}_{14}\text{O}_6$. In aqueous solution these three substances give a blackish-brown coloration with hydrogen sulphide, do not form precipitates with potassium hydroxide, and yield bismuth oxyiodide on addition of potassium iodide.

The following salts of bismuth are prepared by adding the corresponding free acids or the sodium salts to the aqueous solution of

bismuth nitrate and mannitol; a precipitate is not formed on addition of nitric acid or sodium nitrate.

Bismuth salicylate, $(\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2)_3\text{Bi}\cdot 2\text{H}_2\text{O}$, forms a thick, white, crystalline meal, is sparingly soluble in alcohol, and on prolonged washing is converted into the basic salt,



the *camphorate*, $(\text{C}_{10}\text{H}_{14}\text{O}_4)_3\text{Bi}\cdot\text{C}_{10}\text{H}_{16}\text{O}_4$, is obtained as a thick, white, crystalline meal; *phthalate*, $(\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2)_3\text{Bi}$, crystallises in white, quadratic plates, and is not decomposed by potassium hydroxide; *citrate*, $\text{OH}\cdot\text{C}_3\text{H}_4(\text{CO}_2)_3\text{Bi}$, forms a white, crystalline precipitate; *benzoate*, $(\text{C}_6\text{H}_5\cdot\text{CO}_2)_3\text{Bi}$, crystallises in white needles; *oxalate*, $(\text{C}_2\text{O}_4)_3\text{Bi}\cdot 2\text{H}_2\text{O}$, forms a white, micro-crystalline precipitate; *nitrite*, $\text{BiO}\cdot\text{NO}\cdot\frac{1}{2}\text{H}_2\text{O}$, is obtained as a yellowish-white precipitate, which decomposes above 60° and dissolves readily in hydrochloric acid, forming a solution remaining clear on dilution; *hypophosphite*, $\text{Bi}(\text{H}_2\text{PO}_2)_3$, forms a white, crystalline precipitate, which decomposes slowly when dry, more quickly when moist, with separation of metallic bismuth; *phosphite*, $\text{Bi}_2(\text{HPO}_3)_3\cdot 3\text{H}_2\text{O}$, crystallises in white, tetragonal needles and is not decomposed by potassium hydroxide; *phosphate*, $\text{BiPO}_4\cdot 3\text{H}_2\text{O}$, forms a white, gelatinous precipitate; *borate*, $\text{BiBO}_3\cdot 2\text{H}_2\text{O}$, is obtained as a white, fine-granular precipitate, and does not react with potassium hydroxide or iodide; *ferrocyanide*, $\text{Bi}_4[\text{Fe}(\text{CN})_6]_3\cdot 2\text{K}_4\text{Fe}(\text{CN})_6$, forms a yellow, amorphous precipitate, which becomes green and crystalline when dried, and does not react with potassium hydroxide or iodide.

With the exceptions mentioned, these bismuth salts are blackened by hydrogen sulphide and are decomposed by potassium hydroxide and iodide. G. Y.

Compounds of Mercuric Chloride and Alcohols with Dicyclopentadiene. KARL A. HOFMANN and E. SEILER (*Ber.*, 1906, 39, 3187—3190. Compare Hofmann and Sand, *Abstr.*, 1900, i, 384).—The authors have investigated the action of mercuric chloride on alcoholic solutions of dicyclopentadiene.

The compound $\text{HgCl}_2\cdot\text{C}_{10}\text{H}_{12}\cdot\text{OMe}$, prepared from mercuric chloride, methyl alcohol, and dicyclopentadiene, separates from a mixture of methyl alcohol and water in faintly yellow needles and melts at 133° . When acted on by hydrochloric acid, it regenerates dicyclopentadiene. When its solution in concentrated sulphuric acid is warmed, it assumes a pink coloration with a green fluorescence.

The compound $\text{HgCl}_2\cdot\text{C}_{10}\text{H}_{12}\cdot\text{OEt}$, prepared from mercuric chloride, ethyl alcohol, and dicyclopentadiene, crystallises from aqueous alcohol in prisms and melts at 98° . From the stability of the compound on long exposure under diminished pressure and also at 90° , as well as from the cryoscopic determinations made in benzene solution, it is deduced that the alcohol is not present in the molecule as alcohol of crystallisation. The presence of an unsaturated linking in the molecule is shown by the behaviour of the compound towards permanganate.

The compound $\text{HgCl}_2\cdot\text{C}_{10}\text{H}_{12}\cdot\text{O}\cdot\text{C}_5\text{H}_{11}$, obtained from amyl alcohol, mercuric chloride, and dicyclopentadiene, is a heavy oil and solidifies at about -12° . A. McK.

Action of Hydrogen Bromide on Primary and Secondary Saturated Alcohols. H. FOURNIER (*Bull. Soc. chim.*, 1906, [iii], 35, 621—625).—A regular current of hydrogen bromide may be obtained by allowing bromine to fall, drop by drop, into toluene containing 2 per cent. of its weight of steel wire. The hydrogen bromide so produced is passed through a reflux condenser, then through a U-tube containing yellow phosphorus and a little water, and finally into the appropriate alcohol contained in a flask fitted with a Vigreux column, leading to a condenser. The alcohol is at first heated to within a few degrees of its boiling point, and eventually to such a temperature that the alkyl bromide produced will just distil. The yield is always about 70 per cent.

The following alcohols have been converted into the corresponding alkyl bromides by the above method: ethyl, propyl, *isopropyl*, *isobutyl*, *n*-butyl, *n*-amyl, *isoamyl*, and *isohexyl*. The last four alcohols were prepared by Grignard and Tissier's method (*Abstr.*, 1902, i, 198).

T. A. H.

Organic Nitrates. PETER KLASON and TOR CARLSON (*Ber.*, 1906, 39, 2752—2754).—Assuming the peroxide formula, $\text{OEt}\cdot\text{O}\cdot\text{NO}$, for ethyl nitrate (Baeyer and Villiger, *Ber.*, 1901, 34, 755; Brühl, *Abstr.*, 1898, ii, 362), the formation of alkali nitrate and nitrite on hydrolysis can be accounted for by means of the following reactions: $\text{OEt}\cdot\text{O}\cdot\text{NO} + \text{KOH} = \text{KO}\cdot\text{O}\cdot\text{NO} + \text{EtOH}$ and $\text{OEt}\cdot\text{O}\cdot\text{NO} + \text{KOH} = \text{KO}\cdot\text{NO} + \text{OEt}\cdot\text{OH}$.

The probable formation of an alkyl peroxide has been shown by conducting the hydrolysis in the presence of phenyl hydrosulphide, when an appreciable amount of phenyl disulphide is formed, as would be expected from the equation $\text{RO}\cdot\text{OH} + 2\text{R}'\cdot\text{SH} = \text{R}\cdot\text{OH} + \text{R}'_2\text{S}_2 + \text{H}_2\text{O}$. The formation of the disulphide has been proved with glyceryl trinitrate, cellulose nitrate and ethyl nitrate.

J. J. S.

Crystalline Form of Platinichlorides of Sulphine Derivatives. GREGORI AMINOFF (*Zeit. Kryst. Min.*, 1906, 42, 379—383).—Crystallographic details are given respecting several substances prepared by D. Strömholm (*Abstr.*, 1900, i, 325).

L. J. S.

Preparation of the Chloride of Methionic Acid. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 171935).—Although, as shown by Kohler (*Abstr.*, 1898, i, 68), the action of phosphorus pentachloride on potassium methionate leads to the production of chloromethanesulphonic chloride, yet it has now been found that methionyl chloride may be prepared by treating free methionic acid with the chlorides or oxychloride of phosphorus. The dry acid (100 parts) is gently warmed with 240 parts of phosphorus pentachloride, the oxychloride distilled off, and the residue fractionated under diminished pressure. *Methionyl chloride*, $\text{CH}_2(\text{SO}_2\text{Cl})_2$, is a colourless liquid boiling at 135° under 10 mm. pressure; it is slowly hydrolysed by water, and with aniline in chloroform solution it yields the *anilide*, $\text{CH}_2(\text{SO}_2\cdot\text{NHPh})_2$; this is sparingly soluble in water, but dissolves in dilute aqueous alkalis, being reprecipitated by acids. G. T. M.

Constitution of Paris Green and its Homologues. SAMUEL AVERY (*J. Amer. Chem. Soc.*, 1906, 28, 1155—1164).—A large number of specimens of Paris green prepared in several different ways, with an excess of copper, excess of acetic acid, excess of ammonia, or with an excess of any two of these, were analysed and found to contain between 57.3 and 57.7 per cent. of arsenious oxide [$3\text{CuAs}_2\text{O}_4 \cdot \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ requires $\text{As}_2\text{O}_3 = 58.55$ per cent.]. The formic, propionic, and butyric homologues were also prepared and analysed. The results show that these substances are compounds of copper meta-arsenite and a copper salt of the organic acid combined in a ratio which is usually nearly 3:1, but sometimes approaches 2:1. Between these limits, the crystalline structure and colour do not vary with the composition. Efforts were made to obtain compounds of a ratio 4:1 and 1:1 but without success. It was found that in a series of organic acids, the stronger the acid, the more nearly does the ratio approach 3:1. Thus the formic acid compound is more nearly of this composition than the acetic acid compound, and the latter more so than the propionic homologue. A similar green compound can be obtained with succinic acid, and, in general, such compounds may be formed whenever an acid containing a carboxyl group yields a soluble copper salt and does not form complex ions with copper.

When Paris green of composition approximately 3:1 is boiled with a large excess of solution of arsenious oxide, a product of more exactly 3:1 composition is obtained, but the amount of arsenic never quite reaches that required by the formula $3\text{CuAs}_2\text{O}_4 \cdot \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$. If the boiling is continued, the substance suddenly becomes paler in colour and is converted into anhydrous copper meta-arsenite. By treating Paris green with neutral copper acetate solution, a brown, amorphous powder is obtained which contains a larger proportion of copper than Paris green and is always hydrated. When Paris green is boiled for several hours with water, it is gradually resolved into its components.

On the addition of arsenious oxide solution to a solution of zinc acetate containing a little free acetic acid, a white, granular precipitate is obtained which appears to consist of zinc meta-arsenite crystallised with a small quantity of zinc acetate. The preparation of *zinc meta-arsenite* is described. When zinc butyrate is substituted for the acetate, the precipitate obtained on adding arsenious oxide may contain as much as 10 per cent. of butyric anhydride, but in this case the precipitate contains a considerable quantity of zinc ortho-arsenite. It is evident, therefore, that the stronger acid has a greater tendency to replace arsenious acid in the zinc compounds as well as in those of copper. E. G.

Action of Alkali Carbonates on β -Dibromo- $\alpha\alpha$ -dimethyl Acids. Part I. ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, [iii], 35, 657—664).— β -Dibromo- $\alpha\alpha$ -dimethylbutyric acid is not reduced by zinc and acetic acid, but is reconverted into $\alpha\alpha$ -dimethylvinylacetic acid (this vol., i, 231). On treatment with a dilute aqueous solution of potassium carbonate, it yields β -bromo- $\alpha\alpha$ -dimethylbutyrolactone,

$\begin{array}{c} \text{CHBr} \cdot \text{CMe}_2 \\ | \\ \text{CH}_2 \end{array} \text{---} \text{O} \text{---} \text{CO}$, which crystallises from light petroleum in groups of colourless needles, melts at 47° , and when boiled for two hours with an aqueous solution of potassium carbonate (2 mols.) gives off carbon dioxide and yields *dimethylallyl alcohol*, $\text{CMe}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OH}$, and *β -hydroxy- $\alpha\alpha$ -dimethylbutyrolactone*. The latter crystallises in hygroscopic needles, melts at 31° , and boils at 163° under 15 mm. pressure. The formation of dimethylallyl alcohol in this reaction is assumed to take place in the following way: $\text{CH}_2\text{Br} \cdot \text{CHBr} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H} \rightarrow \text{CH}_2\text{Br} \cdot \text{CHBr} \cdot \text{CHMe}_2 \rightarrow \text{OH} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CMe}_2$. The alcohol is a sweet-smelling, mobile liquid, which boils at 65° under 24 mm. or at 140° under atmospheric pressure; the *acetate* is a liquid of pleasant odour and boils at 152° ; the *phenylcarbamate* crystallises from a mixture of ether and light petroleum in colourless needles and melts at 65° . On bromination, dimethylallyl alcohol yields *$\alpha\beta$ -dibromo- β -methylbutyl alcohol*, which crystallises from light petroleum in colourless needles and melts at $37\text{--}38^\circ$. On oxidation with permanganate, dimethylallyl alcohol yields acetone and oxalic acid.

When *β -bromo- $\alpha\alpha$ -dimethylvalerolactone* is boiled with an aqueous solution of potassium carbonate (2 mols.), the products formed are the *methylpentenol*, $\text{CMe}_2 \cdot \text{CH} \cdot \text{CHMe} \cdot \text{OH}$, an odorous liquid, which boils at 65° under 38 mm. pressure, and *β -hydroxy- $\alpha\alpha$ -dimethylvalerolactone*. The latter, which is the principal product of the reaction, separates from light petroleum in opaque crystals and melts at 80° .

The two *$\beta\gamma$ -dibromo- $\alpha\alpha$ -dimethyl acids* dealt with in the present paper belong to the type $\text{R} \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$, where R may be an alkyl radicle or a hydrogen atom. The acids of the type $\text{CH}_2\text{Br} \cdot \text{CRBr} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$, where R may be aliphatic or aromatic, on treatment with alkali carbonates yield a tertiary alcohol, which undergoes dehydration, so that the final product of the reaction is a diethylenic hydrocarbon. It is suggested that this reaction takes place in the following steps: $\text{CH}_2\text{Br} \cdot \text{CMe}(\text{Br}) \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H} \rightarrow \text{CH}_2\text{Br} \cdot \text{CMe}(\text{CO}_2\text{H}) \cdot \text{CMe}_2\text{Br} \rightarrow \text{CH}_2\text{Br} \cdot \text{CHMe} \cdot \text{CMe}_2\text{Br} \rightarrow \text{CH}_2 \cdot \text{CMe} \cdot \text{CMe}_2\text{Br} \rightarrow \text{CH}_2 \cdot \text{CMe} \cdot \text{CMe}_2 \cdot \text{OH} \rightarrow \text{CH}_2 \cdot \text{CMe} \cdot \text{CMe} \cdot \text{CH}_2$.

The migration of a carboxyl group, which is assumed here, has been observed to occur in the action of phosphoric oxide on phenyl-hydroxypivalic acid.

T. A. H.

Reaction between Silver Nitrate and Organic Halogen Compounds. HANS EULER (*Ber.*, 1906, **39**, 2726—2734. Compare J. Wislicenus, *Abstr.*, 1882, 934; Hecht, Conrad, and Brückner, *ibid.*, 1890, 4; Wildermann, 1892, 399; Lobry de Bruyn and Steger, 1899, i, 744, 745, 849; Burke and Donnan, *Trans.*, 1904, **85**, 555). —The reaction between monochloroacetic acid and silver nitrate, $\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{H} + \text{AgNO}_3 + \text{H}_2\text{O} = \text{AgCl} + \text{OH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} + \text{HNO}_3$, in both aqueous and 45 per cent. alcoholic solution, is bimolecular, and the value of *K* for both solvents at 80° is 0.0018. The constant decreases to a slight extent as the time increases, and this is due to the formation of free nitric acid. The temperature-coefficient is relatively high, as indicated by the following numbers: 1000 *K*, 0.45 at 65° , 0.70 at 70° , and 1.80 at 80° .

The constant for the reaction between ethyl chloroacetate and silver nitrate in 45 per cent. alcohol is $1000 K = 1.4$ at 85° . The constant is considerably increased when sodium chloroacetate is substituted for the free acid, as indicated by the following numbers for $1000 K$. Sodium salt, 1.7 at 65° , 10.0 at 80° ; acid, 0.45 at 65° , 1.80 at 80° .

When sodium nitrate is used, the constant falls to about the same value as when water alone is used. The value $1,000 K$ for the reaction between sodium hydroxide solution and sodium chloroacetate is 25.0 at 80° and 6.0 at 65° , and is increased by the presence of sodium chloride. The reaction between bromoacetic acid and silver nitrate, and also that between sodium bromoacetate and sodium hydroxide solution, take place more readily than in the case of the corresponding chloro-derivatives. The values for $1000 K$ at 65° are bromoacetic acid and silver nitrate 42, sodium bromoacetate and sodium hydroxide 195, and at 35° , ethyl bromide and silver nitrate 85, and ethyl bromide and sodium hydroxide 6.5.

The conclusions that these reactions are preceded by ionisation and the reactions measured are the rates of ionisation are adversely criticised, and the view is expressed that the reaction is due to a complex of the type $\text{Ag} \cdot \text{C}_2\text{H}_5\text{Br}$.

J. J. S.

Condition of Pseudo-acids in Aqueous Solution. HEINRICH LEY and ARTHUR HANTZSCH (*Ber.*, 1906, **39**, 3149—3160).—The authors show that pseudo-acids of the class of aliphatic nitro-compounds, like nitromethane, which have practically a neutral reaction in aqueous solution, do actually, however, undergo slight electrolytic dissociation in aqueous solution; the ionisation in water is never equal to nothing, as was formerly erroneously supposed by Hantzsch and his pupils. The dissociation constant of nitromethane, as deduced from its electrical conductivity in aqueous solution, is less than that of phenol. It is now concluded that there are no abnormal relationships between the affinity constant of nitromethane and the hydrolysis of its sodium salt.

Ethyl nitroacetate, $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, is a pseudo-acid with a stronger tendency to ionisation than nitromethane. Its aqueous solution is distinctly acid, and it may be sharply titrated with sodium hydroxide and phenolphthalein. Determinations of its conductivity showed that it was about ten times as weak an acid as acetic acid. Solutions of its alkali salts have a distinctly alkaline reaction and are not neutral, as was formerly supposed.

Ethyl nitropropionate, $\text{NO}_2 \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$, prepared by converting ethyl nitromalonate into ethyl nitroisossuccinate and then saponifying the latter, boils at 80° under 20 mm. pressure. Its sodium salt crystallises in needles and melts and decomposes at 205° . Determinations of the electrical conductivity of the acid showed that in strength it is of about the same order as carbonic acid. Its sodium salt has an alkaline reaction in aqueous solution, and here again there was no evidence of abnormal hydrolysis.

Dinitroethane, which is a stronger acid than the preceding nitro-

compounds, also forms an alkali salt which undergoes appreciable hydrolysis, the degree of which is greater than that of sodium acetate.

A. McK.

Stability of Aqueous and Alcoholic Solutions of Acetic Anhydride. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and HENRI BARBIER (*Bull. Soc. chim.*, 1906, [iii], 35, 625—629. Compare Abstr., 1905, i, 642).—Five and 10 per cent. solutions of the anhydride in cold water were made and set aside. From these solutions, equal aliquot parts were withdrawn every ten minutes and added to a slight known excess of aniline, which reacted quantitatively with the residual anhydride to form acetanilide. The acetic acid formed was then estimated by titration with normal sodium hydroxide solution in presence of phenolphthalein. The results are tabulated in the original, and show that the rate of hydration of the anhydride is fairly rapid at first and then decreases. It is also the more rapid the greater the initial dilution of the anhydride and the higher the temperature.

The alcoholic solutions contained (a) 10 per cent. of the anhydride or (b) alcohol and anhydride in molecular proportions, and equal aliquot portions were withdrawn at intervals of twenty-four hours and titrated with normal sodium hydroxide solution. It was observed that the amount of solution necessary to neutralise the acetic acid formed was less than the calculated quantity, unless considerable quantities of water were added before titration.

The results are tabulated in the original, and show that after a month esterification is incomplete, even in the solution initially containing anhydride and alcohol in molecular proportion. T. A. H.

Preparation of the Anhydrides of Organic Acids. RUDOLF SOMMER (D.R.-P. 171146).—The anhydrides of organic acids are readily prepared by heating their well-dried salts with silicon fluoride when the volatile anhydrides are distilled off from the mixture. The residue, when treated with sand and sulphuric acid, furnishes a fresh supply of silicon fluoride for the next operation. For example, silicon fluoride is passed into anhydrous sodium acetate at 200—220°, the gas is rapidly absorbed, and as this absorption ceases the acetic anhydride begins to distil over; the excess of silicon fluoride is collected in special condensing vessels. Potassium benzoate when similarly treated yields benzoic anhydride, which is extracted from the mixture with petroleum. G. T. M.

Platinous Salts of Certain Organic Acids containing Sulphur. LUDWIG RAMBERG (*Zeit. anorg. Chem.*, 1906, 50, 439—445).—*Platinous xanthate*, $(\text{OEt}\cdot\text{CS}\cdot\text{S})_2\text{Pt}$, obtained by interaction of potassium platinochloride and potassium xanthate in aqueous solution, occurs in flat, yellow prisms melting at 129—130°. It is insoluble in water, readily soluble in chloroform, and has the normal molecular weight in ethylene dibromide. It does not form additive compounds with hydrogen chloride or ammonia. *Platinous ethylthiolacetate*, $(\text{SEt}\cdot\text{CH}_2\cdot\text{CO}_2)_2\text{Pt}$, obtained by interaction of potassium ethylthiol-

acetate and potassium platinochloride in aqueous solution, occurs in very light green crystals. It is very soluble in boiling water, partly polymerised in glacial acetic acid solution, and combines with 1 and 2 molecules of the halogen acids to form mono- and di-basic acids respectively. It also forms an additive compound with ammonia. *Platinous phenylthiolacetate*, $(\text{SPh} \cdot \text{CH}_2 \cdot \text{CO}_2)_2\text{Pt}$, obtained by interaction of sodium phenylthiolacetate and potassium platinochloride, occurs in very light green needles, melting with decomposition at $225-226^\circ$. It is slightly soluble in water, not polymerised in glacial acetic acid, forms acid additive compounds with the halogen acids, and with ammonia a compound $(\text{SPh} \cdot \text{CH}_2 \cdot \text{CO}_2)_2\text{Pt} \cdot 4\text{NH}_3$, which occurs in small colourless or yellow crystals. *Platinous hydrogen thiodiglycollate*, $(\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2)_2\text{Pt}$, obtained by interaction of potassium platinochloride and potassium hydrogen thiodiglycollate or of platinous chloride and thiolacetic acid in hot concentrated aqueous solution, forms small, practically colourless needles. This compound is a dibasic acid; its acid potassium salt occurs in small, green needles.

It is pointed out that the xanthate differs entirely in its behaviour from the other compounds; this is due in all probability to the presence of two sulphur atoms, one of which is joined directly to platinum. The investigation of the other three salts and their additive compounds is being continued. G. S.

Constitution of Oleic Acid and the Action of Ozone on Fats. ETTORE MOLINARI and E. SONCINI (*Ber.*, 1906, **39**, 2735—2744. Compare Harries and Thieme, this vol., i, 227).—The iodine number 192 for the unsaturated acids obtained from pure linseed oil indicates the presence of acids containing triple linkings in addition to olefinic acids. The unsaturated acids readily combine with ozone, and the "ozone number," like the iodine number, is characteristic for each oil. The number is readily obtained by determining gravimetrically the amount of ozone absorbed by a solution of the oil in acetic acid or in a petroleum of high boiling point.

A simple method for the determination of the amount of ozone in a gaseous mixture is by absorption in olein and noting the increase in weight.

Oleic acid ozonide, $\text{C}_{18}\text{H}_{34}\text{O}_5$, is a colourless, transparent, viscous liquid, heavier than water. It does not absorb iodine and is stable up to a temperature of $80-90^\circ$. When subjected to dry distillation it yields a number of products which have not been completely investigated. When warmed with aqueous sodium hydroxide it yields a neutral product with a pleasant sharp odour and boiling at about 190° . In addition, four acids are produced, namely, *n*-nonylic acid, azealic acid,

an acid, $\begin{array}{c} \text{O} \cdot \text{CH} \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{H} \\ | \\ \text{O} \cdot \text{CH} \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{H} \end{array}$, which yields a soluble calcium salt and *α*-hydroxy-*α*-octyldecoic (hydroxydioctylacetic) acid, $\text{OH} \cdot \text{C}(\text{C}_8\text{H}_{17})_2 \cdot \text{CO}_2\text{H}$, the calcium salt of which is insoluble in water. The last acid is a solid, waxy substance melting at about 37° and distilling at 225° under reduced pressure. The acid $\text{C}_{18}\text{H}_{32}\text{O}_6$ is an oil which

decomposes when distilled under reduced pressure and may be oxidised quantitatively to azelaic acid.

The formation of these four acids is in complete harmony with the view that the double linking in the molecule of oleic acid is in the θ -position (compare Saytzeff, *Abstr.*, 1893, i, 551; Baruch, *Abstr.*, 1894, i, 170; and Lewkowitsch, *J. Soc. Chem. Ind.*, 1897, 16, 391).

J. J. S.

Oleic Acid Ozonide. CARL D. HARRIES and CARL THIEME (*Ber.*, 1906, 39, 2844—2846. Compare this vol., i, 225; Molinari and Soncini, preceding abstract).—The ozonide obtained by the action of ozone on a chloroform solution of oleic acid has the composition $C_{18}H_{34}O_6$ and is termed *oleic acid ozonide peroxide*. When purified by solution in ethyl acetate and precipitation with light petroleum, it forms a water-clear, vitreous product. When washed with water and sodium hydrogen carbonate solution, it yields the normal ozonide, $C_{18}H_{34}O_5$, which can also be prepared by the action of ozone on an acetic acid solution of oleic acid and subsequent precipitation with water and washing with the acid carbonate.

When boiled with water, the peroxide gives a much more intense hydrogen peroxide reaction than the normal ozonide. Both products yield with water, azelaic acid or its half aldehyde and nonylic acid or the corresponding aldehyde.

J. J. S.

Lactonisation of $\alpha\alpha$ -Dimethyl- $\beta\gamma$ -unsaturated Acids. EDMOND E. BLAISE and ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, [iii], 35, 580—588).—When $\alpha\alpha$ -dimethylvinylacetic acid is dissolved in sulphuric acid and the solution is immediately poured into excess of water the principal product is β -hydroxy- $\alpha\alpha$ -dimethylbutyric acid, but if the solution be warmed trimethylethylene is formed. When dimethylvinylacetic acid is treated with hydrobromic acid, the bromine atom is added on, partly in the β - and partly in the γ -position, and the product on treatment with alkali carbonates yields a mixture of trimethylethylene and $\alpha\alpha$ -dimethylbutyrolactone. With hydrogen iodide, the iodine atom takes the β -position and the product on treatment with alkali carbonates yields only trimethylethylene. The latter boils at 37—38°; its *dibromide* melts at 7° and boils at 57° under 14 mm. pressure.

$\alpha\alpha$ -Dimethylbutyrolactone is a liquid with a strong odour, melts at 6° and boils at 84° under 13 mm. pressure. *$\alpha\alpha$ -Dimethylvalerolactone*, obtained by dehydrating dimethylpropenylacetic acid [mol. vol. (calc.) 138.9] with sulphuric acid, or by the action of alkali carbonates on γ -iodo- $\alpha\alpha$ -dimethylvaleric acid, prepared by adding hydrogen iodide to dimethylpropenylacetic acid, crystallises from light petroleum, melts at 52°, and has the mol. vol. 130.44 at 28° (compare Blanc, *Abstr.*, 1905, i, 680). When heated during twelve hours at 300° with an equal weight of potassium cyanide, the lactone yields potassium γ -cyano- $\alpha\alpha$ -dimethylvalerate, and this is converted by hydrochloric acid into *trimethylglutarimide*, which melts at 139° and sublimes readily.

Dimethylisopropenylacetic acid, when warmed with sulphuric acid,

yields first hydroxytrimethylbutyric acid and then tetramethylethylene (Reformatsky and Plesconsoff, Abstr., 1896, i, 128).

β -Bromo- $\alpha\beta$ -trimethylbutyric acid, $\text{CMe}_2\text{Br}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$, obtained by the action of hydrobromic acid on dimethylisopropenylacetic acid, crystallises from a mixture of ether and light petroleum and decomposes at 150° . β -Iodo- $\alpha\beta$ -trimethylbutyric acid, obtained in an analogous manner, forms small crystals and decomposes at 170° . Both these halogen derivatives, when treated with alkali carbonates, yield tetramethylethylene. The latter boils at 72° . The dibromide separates from ether in characteristic quadratic prisms, and melts and decomposes at 92° .

Phenyldimethylvinylacetic acid is not readily attacked by hot sulphuric acid, and the sole product is *phenyltrimethylethylene*. This is a mobile liquid, boils at 83° under 12 mm. and at 189° under atmospheric pressure, yields oily products with bromine or hypochlorous acid, and on oxidation with permanganate furnishes acetone and acetophenone.

Sulphuric acid has no action on benzyldimethylvinylacetic acid. Hydroxyvinylpivalic acid, on treatment with sulphuric acid, furnishes a neutral product, which is not volatile under reduced pressure and may be a polymerised diethylenic hydrocarbon.

The foregoing results show that Fittig's rule for the diagnosis of β -unsaturated acids is not quite generally applicable. Acids of the type $\text{CHR}:\text{CH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ readily yield lactones under these conditions, whilst acids of the type $\text{CH}_2:\text{CR}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ furnish first the corresponding hydroxypivalic acids, and these are then decomposed into carbon dioxide and the unsaturated hydrocarbons. Acids of this class containing an aromatic nucleus are either unattacked by sulphuric acid, or yield a small quantity of the corresponding unsaturated hydrocarbon.

T. A. H.

Abnormal Dehydration of Hydroxyalkylpivalic Esters. II.

EDMOND E. BLAISE and ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, [iii], 35, 589—600. Compare Abstr., 1905, i, 853, and this vol., i, 553).—When ethyl hydroxypivalate (ethyl β -hydroxy- $\alpha\alpha$ -dimethylpropionate) is dehydrated by means of phosphoric oxide, a mixture of ethyl tiglate and ethyl angelate is produced, the former preponderating. A portion of the ethyl tiglate is attacked by the phosphoric acid, yielding ethylene and tiglic acid, whilst the ethyl hydroxypivalate is also partially hydrolysed, and the acid liberated is decomposed, yielding hemipoly lactide.

Ethyl phenylhydroxypivalate (ethyl β -phenyl- $\alpha\alpha$ -dimethylhydracrylate), on treatment with phosphoric oxide, yields ethyl dimethylatropate (ethyl α -phenyl- $\beta\beta$ -dimethylacrylate) as a principal product, with small quantities of ethyl isobutyrate, *phenyl dimethylethylene*, $\text{CMe}_2\cdot\text{CHPh}$, which boils at 72° under 15 mm. pressure, and yields an oily dibromide, and benzaldehyde (the semicarbazide of the latter melts at 235° ; compare Thiele and Stange, Abstr., 1895, i, 251).

Dimethylatropic acid, $\text{CMe}_2\cdot\text{CPh}\cdot\text{CO}_2\text{H}$, separates from warm alcohol in brilliant needles and melts at 151° ; the *methyl* ester forms prismatic crystals, melts at 32° , and boils at 142° under 26 mm. pressure;

the *ethyl* ester is a mobile liquid and boils at 136° under 17 mm. pressure. When treated with bromine in carbon disulphide, the acid furnishes $\alpha\beta$ -dibromo- α -phenyl- β -methylbutyric acid, which crystallises from light petroleum in needles and melts at 105° . Ethyl dimethylatropate, on reduction with sodium, yields α -phenyl- β -methylbutyl alcohol, $\text{CHMe}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{OH}$, a viscous liquid with a thyme-like odour, and boiling at 127° under 15 mm. pressure; the *acetate* is a mobile, pleasant-smelling liquid, and boils at 134° under 15 mm. pressure. On oxidation with permanganate in presence of potassium hydrogen carbonate, dimethylatropic acid yields acetone and a mixture of benzoic and phenylglycollic acids.

Ethyl dimethyltropate is obtained, together with some ethyl- $\alpha\alpha$ -diphenylsuccinate, by condensing acetone with ethyl phenylbromoacetate in presence of zinc. It is a viscous liquid and boils at 152° under 19 mm. pressure. On hydrolysis with potassium hydroxide in alcohol, it furnishes no dimethyltropic acid, but only acetone and phenylacetic acid, and on treatment with phosphoric oxide yields ethyl dimethyltropate, identical with that obtained by the dehydration of ethyl phenylhydroxypivalate (see above).

When benzophenone is condensed with ethyl bromoisobutyrate, a very small quantity of *ethyl β -hydroxy- $\beta\beta$ -diphenylpivalate*,



is formed. This crystallises from light petroleum in superb needles and melts at 101° .

Ethyl benzoylisobutyrate, $\text{CMe}_2\text{Bz}\cdot\text{CO}_2\text{Et}$, obtained by condensing benzonitrile with ethyl bromoisobutyrate in presence of zinc (Abstr., 1901, i, 252), is a slightly mobile liquid and boils at 152° under 20 mm. pressure. When condensed with bromobenzene in presence of zinc, no ethyl diphenylhydroxypivalate is formed.

Benzophenone semicarbazone crystallises from warm alcohol in small needles and melts at 167° .

T. A. H.

A New Case of Tautomerism. LUDWIG KNORR and WILLIAM HICKS (*Ber.*, 1906, 39, 3255—3257).—Ethyl thioacetoacetate (compare Buchka, Abstr., 1890, 28; Michaelis and Philipps, *ibid.*, 582) in alcoholic or benzene solution is converted rapidly into the enolic isomeride, $\text{S}[\text{C}(\text{CO}_2\text{Et})\cdot\text{CMe}\cdot\text{OH}]_2$, which is obtained best by keeping overnight an ethereal solution of the ester containing a trace of sodium hydroxide. It is a transparent oil which passes, slowly of itself, rapidly by shaking with sodium carbonate solution, into the solid ketonic modification.

C. S.

Anhydrides of Dibasic Acids. GERARDUS L. VOERMAN (*Bull. Soc. chim.*, 1906, [iii], 35, 665—666).—It is stated that Blaise and Houillon in a note recently published (*Bull. Soc. chim.*, 1906, [iii], 35, 199) have given the impression that the author's work (Abstr., 1904, i, 287; 1905, i, 13) on the molecular weights of the anhydrides of the dibasic acids showed that these substances were unimolecular, whereas it was shown that, although cryoscopic determinations in phenol gave normal results, ebullioscopic measurements in acetone gave results indicating that the anhydrides of the acids above adipic acid are polymerised.

T. A. H.

Anhydrides of Dibasic Acids. EDMOND E. BLAISE (*Bull. Soc. chim.*, 1906, [iii], 35, 666).—A reply to Voerman (see preceding abstract), in which a detailed consideration of the latter's results is promised in a forthcoming paper on the anhydrides of dibasic acids.

T. A. H.

Decomposition of Malonic Ester Chloride. HERMANN LEUCHS (*Ber.*, 1906, 39, 2641—2643).—The author has shown previously that when carbethoxyglycyl chloride is heated, it forms glycinecarboxylic anhydride with elimination of methyl chloride (this vol., i, 236). Ethyl malonate chloride has now been studied from the same standpoint.

When ethyl malonate chloride was heated for one hour at 125—130°, hydrogen chloride was evolved, but there was no evidence of the formation of ethyl chloride. The residue yielded the compound $C_{13}H_{12}O_8$, which separated from methyl alcohol in yellow prisms and melted at 170—180° (corr.). A determination of its molecular weight by the cryoscopic method in benzene solution gave a value corresponding with the formula quoted.

From methyl malonate chloride, the corresponding methyl compound, $C_{11}H_8O_8$, is formed in an analogous manner. It melts at 184—185° (corr.), and is similar in behaviour to the ethyl compound.

A. McK.

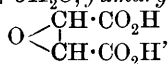
Halogenated Aliphatic Acids. II. WILHELM LOSSEN (*Annalen*, 1906, 348, 261—346. Compare Abstr., 1893, i, 142, and this vol., i, 59).—[With ERICH MENDTHAL.]—The velocity of the conversion of bromosuccinic acid into fumaric acid in the presence of water and at various concentrations (1—3 mol. proportions) has been investigated. The reaction is greatly accelerated by the presence of an alkali hydroxide, even when the solution remained acid after the addition of 1 mol. of the base. From a consideration of the possible configurations of the salts of bromosuccinic acid, it is concluded that the sodium hydrogen salt alone undergoes this decomposition.

[With WALTHER BERGAU.]—Tribromosuccinic acid, prepared by a modification of Petri's method (Abstr., 1879, 373), crystallises in plates melting at 136° and is not hygroscopic; its *aniline* salt, prepared by mixing the ethereal or alcoholic solutions of its constituents, crystallises in prisms. An aqueous solution of the acid is decomposed quantitatively into dibromoacrylic acid, carbon dioxide, and hydrogen bromide. One hundred parts of a saturated solution of dibromoacrylic acid at 90° contains 8.2 parts of the acid.

When tribromosuccinic acid is treated with potassium hydroxide, it is converted quantitatively into dibromomaleic acid, provided that 3 mols. of the base are used for each mol. of the acid. On allowing gaseous ammonia to come in contact with a highly concentrated aqueous solution of tribromosuccinic acid, dibromomaleic acid is also produced, but if the acid is treated with strong aqueous ammonia, bromofumaric acid is formed. If a solution of tribromosuccinic acid in benzene is boiled, dibromomaleic acid is alone formed, a fact which

is not in agreement either with Wislicenus's experimental results or his theoretical views.

[With WALTHER SCHÖRK and MAX NIEHRENHEIM.]—*Chloromalic acid*, $\text{CO}_2\text{H}\cdot\text{CHCl}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, is readily prepared from either sodium maleate or fumarate by adding chlorine water to the aqueous solution of the salt: $\text{C}_4\text{H}_2\text{O}_4\text{Na}_2 + \text{Cl}_2 + \text{H}_2\text{O} = \text{C}_4\text{H}_5\text{O}_5\text{ClNa} + \text{NaCl}$. The acid crystallises in monoclinic needles [$a:b:c = 1.387:1:0.84904$; $\beta = 65^\circ 41'$] melting at 143° and decomposing at a somewhat higher temperature. The *sodium* and *silver* salts are anhydrous, whilst the *barium* salt crystallises with $3\text{H}_2\text{O}$, and the *lead* salt with $2\text{H}_2\text{O}$. The *methyl* ester is an oily liquid. When subjected to dry distillation, chloromalic acid is mainly converted into chloromaleic acid, the same compound being also formed on heating the acid with a saturated solution of hydrochloric acid under pressure. On reduction with a zinc platinum couple in aqueous solution, malic acid is formed. When the aqueous solution is boiled, carbon dioxide, aldehyde, and hydrochloric and tartaric acids are produced, the rate of the decomposition increasing with the dilution: $\text{C}_4\text{H}_5\text{O}_5\text{Cl} + \text{H}_2\text{O} = \text{C}_4\text{H}_6\text{O}_6 + \text{HCl}$; $\text{C}_4\text{H}_5\text{O}_5\text{Cl} = \text{C}_2\text{H}_4\text{O} + \text{CO}_2 + \text{HCl}$. A similar decomposition occurs when potassium hydrogen chloromaleate is boiled in aqueous solution. The normal salt decomposes in a similar manner, but the main reaction is the formation of aldehyde and carbon dioxide. When boiled with an excess (3 mols.) of *N*-potassium hydroxide, a reaction takes place quantitatively according to the following equation: $\text{C}_4\text{H}_5\text{O}_5\text{Cl} + 3\text{KOH} = \text{C}_4\text{H}_4\text{O}_6\text{K}_2 + \text{KCl} + 3\text{H}_2\text{O}$, *fumarylglglycidic acid*,



being produced.

[With HANS DUECK and MAX LEOPOLD.]—*Bromomalic acid*, $\text{CO}_2\text{H}\cdot\text{CHBr}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$,

is prepared by the action of bromine water on an alkaline solution of fumaric acid; the acid forms monoclinic crystals, isomorphous with chloromalic acid and melting at $132\text{--}134^\circ$. The *sodium* salt is anhydrous and decomposes at 100° ; the *barium* salt crystallises with 3 and $4\text{H}_2\text{O}$, whilst the *lead* and *silver* salts are anhydrous. When subjected to dry distillation, carbon dioxide, hydrogen bromide, and bromomaleic acid are formed. If the aqueous solution is boiled, carbon dioxide, aldehyde, and hydrobromic and racemic acids are produced, whilst, as in the case of chloromalic acid, the action of sodium hydroxide leads quantitatively to the formation of fumarylglglycidic acid. When an attempt was made to prepare this acid from barium maleate, a bromomalic acid was obtained, which crystallised with H_2O and melted at $63\text{--}65^\circ$; its salts are identical with those of the anhydrous acid, and on melting it yields the crystals of the latter. If a solution of molecular proportions of the anhydrous acid and water are made in ether or chloroform, the anhydrous acid crystallises out on evaporation, but if the solution is sown with a crystal of the hydrated acid, the latter separates. The decomposition of the hydrated acid in water is similar to that of the anhydrous, but it was found that mesotartaric acid was formed at the same time as racemic acid. The barium salts of both acids behaved in a similar manner when their solutions were

boiled. Both acids were converted into fumarylglcydic acid with equal ease.

[With WALTHER SCHÖRK, MAX NIEHRENHEIM, HANS DUECK, and MAX LEOPOLD.]—Fumarylglcydic acid, prepared either from chloro- or bromo-malic acid, forms prismatic crystals melting at 203° ; its *sodium* salt, $C_4H_3O_5Na \cdot H_2O$, crystallises in plates, the *calcium*, *barium*, and the *lead* salts each crystallise with $2H_2O$, whilst the *silver* salt is anhydrous and explosive. The *methyl* ester, $O < \begin{smallmatrix} CH \cdot CO_2Me \\ | \\ CH \cdot CO_2Me \end{smallmatrix}$, prepared from the silver

salt and methyl iodide, crystallises in needles melting at 73° , and reacts neither with acetyl chloride nor with phenylcarbimide; hence no hydroxyl group is present. The *acid chloride*, prepared from the acid and phosphorus pentachloride, forms scaly crystals melting at 53° and boiling at 90 — 93° under 40 mm. pressure. The *diphenyl ester*, $C_2H_2O(CO_2Ph)_2$, prepared from the acid chloride and phenol, forms crystals melting at 133° . The *amide*, $C_2H_2O(CO \cdot NH_2)_2$, prepared from the methyl ester and alcoholic ammonia, is a microcrystalline solid melting and decomposing at 225° .

On boiling the fumarylglcydic acid with water, carbon dioxide, aldehyde, and racemic and mesotartaric acids are formed. Concentrated hydrochloric and hydrobromic acids convert the acid into the corresponding halogen malic acids; with ammonia, it combines to form aminomalic acid.

[With ERICH MENDTHAL.]—When aqueous solutions of bromofumaric or bromomaleic acids are boiled, they are decomposed into carbon dioxide, aldehyde, and propargylic acid. A similar decomposition occurs if the normal sodium or sodium hydrogen salts are heated in aqueous solution, but in the presence of excess of alkali hydroxide, on the other hand, acetylenedicarboxylic acid is the main product, a portion afterwards decomposing into propargylic acid. Under all conditions, bromofumaric acid decomposes more rapidly than bromomaleic acid; the normal salts decompose most readily, whilst the free acids and the hydrogen salts are relatively stable.

On reducing either of the acids with sodium amalgam or with zinc, fumaric and succinic acids are produced.

[With ADOLF TREIBICH.]—Anhydrous acetylenedicarboxylic acid is prepared by treating the ethereal solution of the hydrated acid with calcium chloride. When a concentrated aqueous solution of the acid is treated with the calculated quantity of bromine vapour, it is converted quantitatively into dibromofumaric acid together with a small quantity of dibromomaleic acid. Acetylenedicarboxylic acid is easily oxidised by permanganate to oxalic acid and carbon dioxide.

The action of bromine on a dilute aqueous solution of acetylenedicarboxylic acid is very complicated, and is represented by the following equations: $C_4H_2O_4 + 4H_2O + 5Br_2 = 4CO_2 + 10HBr$; $C_4H_2O_4 + 4H_2O + 3Br_2 = 2C_2H_2O_4 + 6HBr$; $C_4H_2O_4 + HBr = C_4H_3O_4Br$; $C_4H_2O_4 + Br_2 = C_4H_2O_4Br_2$.

[With WALTHER BERGAU.]—The action of chlorine on acetylenedicarboxylic acid and of chlorine or bromine on sodium acetylenedicarboxylate was investigated under various conditions, but in no case was a simple reaction observed.

K. J. P. O.

Preparation of Peroxide Acids from the Anhydrides of Dibasic Acids. FREDERICK STEAINS & Co. (D.R.-P. 170727).—Peroxide acids having pronounced antiseptic and germicidal properties are produced on shaking the anhydrides of the dibasic acids with a dilute aqueous solution of hydrogen peroxide until a precipitate is produced. Peroxide-phthalic acid, a substance already described, can be prepared in this way, and the reaction takes place equally readily with succinic and glutaric anhydrides.

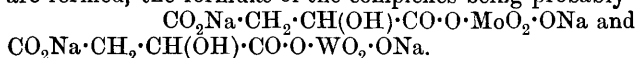
Peroxide succinic acid, $O_2(CO \cdot CH_2 \cdot CH_2 \cdot CO_2H)_2$, separates in colourless tabular crystals slightly soluble in water, alcohol, ethyl acetate, acetic acid, or ether, and insoluble in chloroform or benzene. Water slowly hydrolyses it, yielding molecular proportions of succinic acid and succinic peracid, $CO_2H \cdot CH_2 \cdot CH_2 \cdot CO \cdot O \cdot OH$.

Peroxide glutaric acid, $O_2(CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H)_2$, is prepared similarly by shaking glutaric anhydride for half an hour with 7.8 per cent. aqueous hydrogen peroxide at 30°. G. T. M.

Solubility of Alkaline Earth Malates in Water. H. CANTONI and M. BASADONNA (*Bull. Soc. chim.*, 1906, [iii], 35, 727—737. Compare Abstr., 1904, i, 142).—Strontium malate is the most soluble of the three salts and its solubility increases greatly with rise of temperature. The least soluble salt is calcium malate, and its solubility diminishes as the temperature is increased. The solubility of barium malate is intermediate between that of the calcium and strontium salts and increases very slightly with rise of temperature. The experimental results are tabulated in detail in the original, which also gives a number of solubility curves for the three salts, and details of the methods employed in conducting the experiments and in estimating malic acid. T. A. H.

Increase and Reversal of Rotation. I. Complex Molybdbl and Tungstyl Malates. HERMANN GROSSMANN and HEINZ PÖTTER (*Zeit. physikal. Chem.*, 1906, 56, 577—604. Compare this vol., ii, 211; also Itzig, Abstr., 1901, i, 580).—The rotatory power of solutions containing malic acid and ammonium molybdate, sodium molybdate, or sodium tungstate varies often in a peculiar manner when the concentration and the temperature are altered. The authors have made an extensive study of these variations, their measurements covering the following molecular combinations: (1) 1 mol. $C_4H_6O_5$ + 0.5 mol. $(NH_4)_2MoO_4$ (compare Grossmann and Pötter, Abstr., 1904, ii, 153); (2) 1 mol. $C_4H_6O_5$ + 0.5 mol. Na_2MoO_4 ; (3) 1 mol. $C_4H_6O_5$ + 1 mol. Na_2MoO_4 ; (4) 1 mol. $C_4H_6O_5$ + 1.5 mols. Na_2MoO_4 ; (5) 1 mol. $C_4H_6O_5$ + 2 mols. Na_2MoO_4 ; (6) 1 mol. $C_4H_6O_5$ + 4 mols. Na_2MoO_4 ; (7) 1 mol. $C_4H_6O_5$ + 1 mol. Na_2MoO_4 + 1 mol. MoO_3 ; (8) 1 mol. $C_4H_6O_5$ + 0.5 mol. Na_2WO_4 ; (9) 1 mol. $C_4H_6O_5$ + 1 mol. Na_2WO_4 ; (10) 1 mol. $C_4H_6O_5$ + 1.5 mols. Na_2WO_4 ; (11) 1 mol. $C_4H_6O_5$ + 2 mols. Na_2WO_4 . The observations indicate that the peculiar variations of rotation are in some cases due to the formation of molybdbl and tungstyl dimalates, which are highly active complexes and are but slightly affected by changes of concentra-

tion and temperature. In other cases molybdyl and tungstyl malates are formed, the formulæ of the complexes being probably



The rotation of the molybdyl malate is at the ordinary temperature but little affected by change of concentration, but with rise of temperature it decreases regularly and markedly at all concentrations. In the case of the tungstyl malate, dilution and rise of temperature both produce a marked increase in rotation. When 1 molecule of malic acid is mixed with more than 1 molecule of sodium molybdate or tungstate, complexes are formed, which are sometimes dextrorotatory, sometimes levorotatory, and which are very sensitive to changes of concentration and temperature. The molybdyl complexes of this kind appear to be completely resolved at high dilution into the 1 : 1 salt and inactive sodium molybdate: this splitting up of the higher complex is not quite so definite in the case of the tungstyl compounds. That so many cases of maxima, minima, and reversal of rotation have been observed by the authors is probably due to the formation in the concentrated solutions of slightly stable additive products, characterised by rotations of opposite sign.

J. C. P.

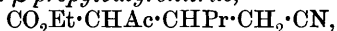
Preparation of Mercury Cholates. J. D. RIEDEL (D.R.-P. 171485).—Mercury cholates are not easily obtained by the double decomposition between cholic acid and the inorganic mercury salts, for in these cases the product is either colloidal or contains excess of the corresponding mercury oxide. Either mercurous or mercuric cholate may, however, be produced readily by employing the mercury salt of an organic acid such as acetic acid. A 5 to 10 per cent. aqueous solution of a soluble cholate is introduced, with vigorous stirring, into a solution of mercurous or mercuric acetate, when the corresponding mercury salt is deposited as a yellowish-white precipitate which can be readily collected and dried.

Mercurous cholate, $\text{C}_{24}\text{H}_{39}\text{O}_5\text{Hg}$, is a yellowish-white, insoluble powder, decomposed by alkalis or alcohol. *Mercuric cholate*, $(\text{C}_{24}\text{H}_{39}\text{O}_5)_2\text{Hg}$, is similar in appearance, but rather more soluble, particularly in acidified water or in aqueous solutions of sodium or potassium chloride; it is also decomposed by alcohol.

G. T. M.

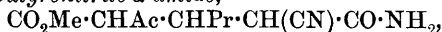
New Derivatives of δ -Ketonic Acids. ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1906, 41, 842—861. Compare Abstr., 1898, i, 274; 1900, i, 52, 111; 1901, i, 341, 630; 1902, i, 819; 1903, i, 736; 1905, i, 821).—The interaction of molecular proportions of ethyl acetoacetate, ethyl cyanoacetate, and *n*-butaldehyde in presence of ammonia yields the ammonium derivative of propyldicyanodioxypyridine (Abstr., 1902, i, 819) and γ -carbethoxy- γ -acetyl- β -propylbutyronitrile- α -amide, $\text{CO}_2\text{Et}\cdot\text{CHAc}\cdot\text{CHPr}\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{NH}_2$, which crystallises from water in shining, colourless prisms, melts at 205—206°, and dissolves in alcohol or acetic acid. It has a neutral reaction, does not absorb bromine and is soluble in sodium hydroxide solution with evolution of ammonia. When heated with excess of

barium hydroxide solution, it yields 2 mols. of ammonia and γ -carbethoxy- γ -acetyl- β -propylbutyric acid (1), which forms a soluble barium salt. On heating with hydrochloric acid of sp. gr. 1.19, it yields γ -carbethoxy- γ -acetyl- β -propylbutyronitrile,



which crystallises from water in long, colourless needles, or from alcohol in prisms, melts at 125—126°, has a neutral reaction, and reduces permanganate. When heated with 60 per cent. sulphuric acid, it gives γ -carbethoxy- γ -acetyl- β -propylbutyric acid (?).

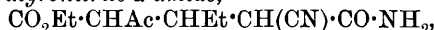
If the ethyl acetoacetate employed in the above reaction is replaced by the corresponding methyl ester, there is obtained γ -carbmethoxy- γ -acetyl- β -propylbutyronitrile- α -amide,



which separates from water in crystals melting at 248—249°.

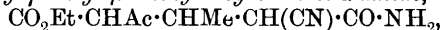
When mixed in molecular proportions, propaldehyde, ethyl acetoacetate, and ethyl cyanoacetate in presence of ammonia yield (1) the ammonium derivative of dicyanodioxymethylpyridine, (2) a compound

which is probably $\text{NH}\langle\begin{smallmatrix} \text{CMe}\cdot\text{C}(\text{CO}_2\text{Et}) \\ \text{CO}—\text{C}(\text{CN}) \end{smallmatrix}\rangle\text{CEt}$, and (3) γ -carbethoxy- γ -acetyl- β -ethylbutyronitrile- α -amide,



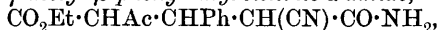
which separates from water in crystals melting at 199—200°, and, on boiling with hydrochloric acid, yields γ -carbethoxy- γ -acetyl- β -ethylbutyronitrile (?), $\text{CO}_2\text{Et}\cdot\text{CHAc}\cdot\text{CHEt}\cdot\text{CH}_2\cdot\text{CN}$, crystallising from water in long needles melting at 92—94°, and dissolving in ether or alcohol.

Acetaldehyde, ethyl acetoacetate, ethyl cyanoacetate and ammonia yield methyl dicyanoglutaconimide, ethyl hydrocollidinedicarboxylate, and γ -carbethoxy- γ -acetyl- β -methylbutyronitrile- α -amide,



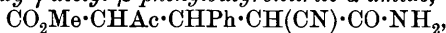
which melts at 212—213° and is soluble in alcohol or water.

γ -Carbmethoxy- γ -acetyl- β -phenylbutyronitrile- α -amide,



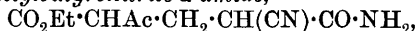
obtained with other products by the interaction of benzaldehyde, ethyl acetoacetate, methyl or ethyl cyanoacetate, and ammonia, crystallises from alcohol in shining, acicular prisms melting at 225—226° and exhibits characters resembling those of the corresponding compounds prepared from aliphatic aldehydes. When heated with hydrochloric acid of sp. gr. 1.19 in presence of alcohol, it yields γ -carbethoxy- γ -acetyl- β -phenylbutyronitrile, which melts at 152—154° and is soluble in ether.

γ -Carbmethoxy- γ -acetyl- β -phenylbutyronitrile- α -amide,



forms heavy, colourless crystals melting at 234—235° and dissolves in water or alcohol.

The interaction of formaldehyde, ethyl acetoacetate, and ethyl cyanoacetate in presence of ammonia yields only a small proportion of γ -carbethoxy- γ -acetyl- β -phenylbutyronitrile- α -amide,



which crystallises in short, heavy prisms melting at 178—180°, the main product being a dicyano-pyridine derivative.

T. H. P.

Synthetical Experiments with *d*-Gluconic Acid. II. CARL PAAL and FRANZ HÖRNSTEIN (*Ber.*, 1906, **39**, 2823—2827. Compare this vol., i, 400).—The lactone of tetra-acetyl-*d*-gluconic acid is obtained as a transparent, faintly yellow-coloured, gummy mass, giving correct results on analysis if care be taken to avoid the use of alcohol in isolating it. It is sparingly soluble in hot water and in benzene solution has $[\alpha]_D + 70.86^\circ$ at 21° . The experimental methods have been improved so as to prepare 1 : 1-diphenyl-*d*-sorbitol in a crystalline form melting at 157 — 160° ; the cold supersaturated solutions in water and alcohol have $[\alpha]_D + 71.25^\circ$ and $+ 74.75^\circ$ respectively at 25° .

E. F. A.

Synthetical Experiments with *d*-Galactonic Acid. CARL PAAL and ERICH WEIDENKAFF (*Ber.*, 1906, **39**, 2827—2833. See preceding abstract).—*Tetra-acetyl-d-galactonic lactone*, prepared by heating the lactone with acetic anhydride, is obtained as a transparent, tough gum having $[\alpha]_D - 1.04^\circ$ at 20° ; the product obtained by acetylating at 50 — 60° has $[\alpha]_D - 8.5^\circ$ at 20° . 1 : 1-Diphenyl-*d*-galactohexitol, obtained by heating the acetyl-lactone, dissolved in benzene, with magnesium phenyl bromide crystallises in ball-like aggregates of colourless, faintly-glistening needles melting at 157 — 160° and containing H_2O . It is less soluble in water and more so in alcohol than diphenylsorbitol. The supersaturated solution in water has $[\alpha]_D + 72.9^\circ$ at 20° , and in alcohol $[\alpha]_D + 56.23^\circ$ at 20° . A by-product of the action of magnesium phenyl bromide is described melting at 93 — 97° and yielding, when heated with potassium hydroxide, crystals melting at 98 — 100° which show $[\alpha]_D - 106.4^\circ$ at 20° .

E. F. A.

Physiological Relationships of the Proteids containing Sulphur. IV. ERNST FRIEDMANN and JULIUS BAER (*Beitr. chem. Physiol. Path.*, 1906, **8**, 326—331. Compare Abstr., 1902, i, 731; 1903, i, 75, 301; 1904, i, 165).—A specimen of pure proteid cystein or α -amino- β -thiolactic acid disulphide, when heated in the form of its hydrochloride with water at 145° for 1.5 hours and then reduced with tin and hydrochloric acid, yields α -thiolactic acid. The formation of this acid is not due, as suggested by Mörner (*Abstr.*, 1904, i, 836), to the presence of an isomeric cystein in the natural product, but is formed from the pure disulphide of α -amino- β -thiolactic acid, probably through the intermediate formation of pyruvic acid, as this is known to yield a product with hydrogen sulphide which on reduction gives α -thiolactic acid.

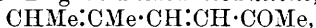
J. J. S.

Zinc Formaldehydesulphoxylate. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 172217).—Sodium formaldehydesulphoxylate was formerly isolated by the fractional crystallisation from the other substances produced by the interaction of formaldehyde and sodium hyposulphite. It is now found that formaldehydesulphoxylic acid forms a sparingly soluble zinc salt which is readily separated from the sulphide present. The separation is best effected by treating a solution of zinc formaldehydesulphite with sodium carbonate in accordance with the following equation: $2ZnS_2O_4, 2CH_2O$

+ $\text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O} = 2\text{ZnSO}_4 \cdot \text{CH}_2\text{O} \cdot \text{H}_2\text{O} + 2\text{NaHSO}_4 \cdot \text{CH}_2\text{O} + \text{CO}_2$. A solution of zinc hyposulphite, ZnS_2O_4 (100 grams) is treated with formaldehyde until it loses its power of reducing indigotinsulphonic acid in the cold, and then 25 grams of dry sodium carbonate are added. The new zinc salt, which separates slowly, is washed and dried; it is a crystalline substance which is stable in the air and which, on digestion with aqueous sodium carbonate, yields a solution of sodium formaldehydesulphoxylate.

G. T. M.

Condensation of Tiglic Aldehyde with Acetone. FRITZ DAUTWITZ (*Monatsh.*, 1906, 27, 773—776).—Tiglic aldehyde, prepared by heating a mixture of acetaldehyde and propaldehyde with sodium acetate solution, condenses with acetone in aqueous sodium hydroxide solution at 5—10°, forming an unsaturated ketone,



which is obtained as a colourless, strongly refracting, mobile oil. It has a characteristic aromatic odour, boils at 92—93° under 12 mm. pressure, is rapidly oxidised by air forming a resin, and forms an *additive* compound with 2 mols. of bromine. The *oxime*, $\text{C}_{18}\text{H}_{19}\text{ON}$, crystallises from light petroleum and melts at 71°, forming a viscid, colourless, strongly refracting oil, which boils at 140—141° under 13 mm. pressure.

G. Y.

Oxidation of Acyloins of the Fatty Series: some α -Diketones and their Derivatives. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1906, [iii], 35, 650—654. Compare Abstr., 1905, i, 573, and this vol., i, 782, 783, 784).—The authors confirm Ponzio's observation (Abstr., 1901, i, 452) that acyloins are not readily converted into α -diketones by the usual oxidising agents. They find, however, that yields of 50 per cent. and upwards of the diketones can be obtained by the application of Sabatier and Senderens' catalytic process (Abstr., 1903, i, 454, and 1905, i, 254) to the acyloins. The authors now find that the statement formerly made (Locquin, Abstr., 1905, i, 20), that the higher α -diketones which do not contain the $\text{CH}_3\cdot\text{CO}$ group do not form sodium hydrogen sulphite compounds, is inaccurate; the compounds are, however, unstable and difficult to isolate in these cases.

Diisobutyryl has a sp. gr. 0.912 at 4°/0° and boils at 144—145°. The *monoxime* boils at 135° under 10 mm. pressure, and the *dioxime* crystallises from boiling benzene and melts at 171.5°. When *diisobutyryl* is treated with magnesium methyl iodide, a *product* is obtained, which boils at 75—80° under 11 mm. pressure, and may have the constitution $\text{COPr}^\beta \cdot \text{CMePr}^\beta \cdot \text{OH}$. With magnesium phenyl bromide, a liquid is produced, which boils at 137° under 11 mm. pressure and may consist of the *substance* $\text{COPr}^\beta \cdot \text{CPhPr}^\beta \cdot \text{OH}$, with a trace of its dehydration product, $\text{COPr}^\beta \cdot \text{CPh}:\text{CMe}_2$.

T. A. H.

Influence of some Mineral Matters on the Liquefaction of Starch. JULES WOLFF and AUGUSTE FERNBACH (*Compt. rend.*, 1906, 143, 363—365).—It was previously shown (*ibid.*, May 15, 1906) that the lime present in starch has considerable influence on the viscosity. Experiments with starch, previously washed until nearly

free from calcium and magnesium, showed that ammonia, sodium carbonate, magnesium carbonate, and calcium carbonate have about the same effect, whilst alumina is without action.

When starch containing the usual bases is treated with sulphuric or phosphoric acid until about neutral (methyl-orange), it very readily loses its viscosity when heated under pressure. N. H. J. M.

Mechanism of the Influence of Acids, Bases, and Salts in the Liquefaction of Starch Paste. AUGUSTE FERNBACH and JULES WOLFF (*Compt. rend.*, 1906, **143**, 380—383. Compare Abstr., 1904, i, 211, 374; 1905, i, 164, 574, 624; preceding abstract). When starch paste is made neutral to methyl-orange by the addition of sulphuric acid and then heated at 120°, its viscosity is very greatly diminished, but if disodium hydrogen phosphate is added to the neutralised paste before heating, the viscosity is increased, and becomes equal to that of the original paste when the quantity of the salt added is two and a half times that of the equivalent of the acid. The addition of neutral salts, such as magnesium or calcium sulphate or of sodium dihydrogen phosphate, to the neutralised starch paste effects no change in its viscosity, nor is the viscosity of the original paste changed by the addition of disodium hydrogen phosphate or of sodium dihydrogen phosphate. The effect of sodium hydroxide in retarding the liquefaction of neutralised starch paste is much more marked than that of disodium hydrogen phosphate. It follows, therefore, that the liquefaction of neutralised starch paste is partly due to the transformation of the secondary phosphates present in the starch into primary phosphates, that it is not affected by the addition of salts neutral to methyl-orange, but is retarded by the addition of salts alkaline to this reagent, and checked altogether by traces of free alkali.

M. A. W.

Starchy Substances studied by the aid of our knowledge of the Colloidal State. G. MALFITANO (*Compt. rend.*, 1906, **143**, 400—403).—A theoretical paper. Fernbach has shown that starch contains 0.2 per cent. of phosphorus in the form of phosphates even after maceration with hydrochloric acid (Abstr., 1904, i, 294); the author therefore regards a clear starch solution as a colloidal solution in which the granules are formed of starch molecules grouped round the :PO_4^- ion, $[(\text{C}_6\text{H}_{10}\text{O}_5)_n\text{PO}_4]^-$; the composition varying with the nature of the free electrolytes in the liquid medium, and subject to the laws already established in the case of a colloidal solution of ferric hydroxychloride (compare Abstr., 1905, ii, 459; this vol., ii, 33, 450, 526).

M. A. W.

Action of Acyl Chlorides on Mixtures of Amines. FRANK B. DAINS (*J. Amer. Chem. Soc.*, 1906, **28**, 1183—1188).—This investigation was carried out with the object of ascertaining whether, when a mixture of two amines in molecular proportions is treated with an acyl chloride, any preference is shown as to the amine attacked, and also of determining the conditions which govern any such preference. The results show that when there is any appreciable difference of basicity

between the two amines, the acyl derivative of the more negative is largely or exclusively produced together with the salt of the more positive amine. E. G.

Compounds of Chromium Tetroxide with Ethylenediamine and Hexamethylenetetramine. KARL A. HOFMANN (*Ber.*, 1906, **39**, 3181—3184).—*Ethylenediamine chromate*, $\text{H}_2\text{CrO}_4 \cdot \text{C}_2\text{H}_8\text{N}_2$, prepared by the addition of ethylenediamine hydrate to an aqueous solution of chromic acid, forms orange-coloured, tetragonal plates, and is sparingly soluble in water.

The compound $\text{CrO}_4 \cdot \text{C}_2\text{H}_8\text{N}_2 \cdot 2\text{H}_2\text{O}$, prepared by cooling in ice the filtrate obtained from a mixture of chromic acid, water, and ethylenediamine hydrate and then adding hydrogen peroxide, forms a glistening, greyish-green, crystalline powder, which deflagrates on heating.

The compound $\text{CrO}_4 \cdot \text{C}_6\text{H}_{12}\text{N}_4$, prepared in a similar manner from hexamethylenetetramine, separates in "reddish-brownish-yellow" hexagonal crystals. When heated it deflagrates. A. McK.

Ethylene- and Propylene-diamine Compounds of Palladium. ALEXANDER GUTBIER and M. WOERNLE (*Ber.*, 1906, **39**, 2716—2720. Compare Abstr., 1905, i, 584, 876; ii, 534; this vol., i, 244, 402).—When an aqueous solution of ethylenediamine or propylenediamine is added to one of a palladous haloid, rose- or flesh-coloured precipitates are obtained, having the composition $\text{PdD}_2\text{X}_2 \cdot \text{PdX}_2$ (where D is the diamine and X is chlorine or bromine). They are soluble in excess of the base, and from the yellow solutions dilute halogen acids precipitate yellow needles of the palladosammines.

Palladous ethylenediamine chloride, PdDCl_2 , *bromide*, PdDBr_2 , *iodide*, PdDCl_2 , and the corresponding propylenediamine compounds, dissolve in concentrated halogen acids, forming dark-coloured solutions, from which, on cooling, substances of the preceding type separate. Substances of the type $\text{PdX}_2 \cdot \text{D} \cdot 2\text{HX}$ have been prepared, and are capable of combining with two atoms of halogen to form compounds of the type $\text{PdX}_4 \cdot \text{D} \cdot 2\text{HCl}$. C. S.

Synthesis of Hydroxy- and Diamino-acids. III. $\alpha\alpha$ -Diaminoazelaic Acid, $\alpha\beta$ -Diaminobutyric Acid, and β -Amino- α -hydroxybutyric Acid. CARL NEUBERG and MAX FEDERER (*Chem. Centr.*, 1906, ii, 764—766; from *Biochem. Zeit.*, 1, 282—298. Compare Abstr., 1905, i, 687).—When treated with bromine in presence of phosphorus, azelaic acid yields $\alpha\alpha$ -dibromoazelaic acid in the form of a yellow, non-crystallisable oil. When heated with concentrated ammonia and ammonium carbonate at 120—125°, this yields $\alpha\alpha$ -diaminoazelaic acid in the form of microscopic crystals, which dissolve in hot water and are readily soluble in alkali hydroxides or mineral acids. It forms insoluble copper, silver, mercury, and lead salts, and combines with phenylcarbimide to form a crystalline phenylhydantoic acid, which melts at about 120°; the diethyl ester is an oil.

$\alpha\beta$ -Diaminobutyric acid was obtained from $\alpha\beta$ -dibromobutyric acid in a similar manner in 24 per cent. yield. With phenylcarbimide, it yields a crystalline compound, $\text{C}_{18}\text{H}_{20}\text{O}_4\text{N}_4$, melting at 238°. With

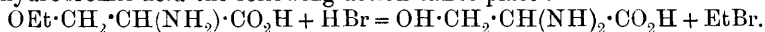
picric acid it yields a picrate, $C_{10}H_{13}O_9N_5 \cdot 2H_2O$, which is hygroscopic and decomposes at about 90° .

When the product obtained by the action of concentrated ammonia is kept for some time, it deposits rhombic crystals of *β -amino- α -hydroxybutyric acid*. Iminobutyric acid is probably formed as an intermediate product, and this then combines with water. It yields a copper salt, $NH_2 \cdot CHMe \cdot CH \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ O \cdot Cu \end{smallmatrix} O$, and with *α -naphthylcarbimide* it gives the crystalline *α -naphthylhydantoic acid*, which decomposes at about 170° .

H. M. D.

A New Synthesis of Serine. HERMANN LEUCHS and WALTER GEIGER (*Ber.*, 1906, **39**, 2644—2649).—The authors describe a third method of synthesising serine, the acid having been formerly synthesised by Erlenmeyer, jun. (*Abstr.*, 1903, i, 29) and by E. Fischer and Leuchs (*Abstr.*, 1903, i, 12).

When chloroacetal, $CH_2Cl \cdot CH(OEt)_2$, is heated with sodium ethoxide it forms ethoxyacetal, $OEt \cdot CH_2 \cdot CH(OEt)_2$, which, when boiled with dilute sulphuric acid, is converted into ethoxyacetaldehyde, $OEt \cdot CH_2 \cdot CHO$. The isolation of this product from the reaction mixture was not necessary, since the latter may be submitted directly to the cyanohydrin reaction by consecutive treatment with ammonia, hydrogen cyanide, and hydrochloric acid, when *β -ethoxy- α -alanine*, $OEt \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$, is formed. The latter compound need not be isolated, since when the reaction mixture is boiled with concentrated hydrobromic acid the following action takes place :



The yield of serine obtained in this manner is 35—40 per cent. of the theoretical, calculated on the ethoxyacetal used.

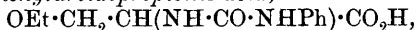
Various derivatives of *β -ethoxy- α -alanine*, serine, and ethoxyacetaldehyde are described.

γ -Phenyl- α -hydroxymethylhydantoin, $C_{10}H_{10}O_3N_2$, prepared by evaporating to dryness a mixture of the alkaline solution of *β -hydroxy- α -phenylureidopropionic acid* and hydrochloric acid, separates from water in needles and melts at 168 — 169° (corr.).

Ethyl carboxymethylserine, $CO_2Me \cdot NH \cdot CH(CH_2 \cdot OH) \cdot CO_2Et$, was prepared as follows: a current of dry hydrogen chloride was passed through an ethyl-alcoholic solution of serine until the latter had dissolved and the mixture then heated for one hour at 100° . The free ethyl serine was then liberated from the resulting hydrochloride and treated with a mixture of methyl chlorocarbonate and sodium carbonate. Ethyl carboxymethylserine is a viscid oil, which boils at 181 — 182° under 12 mm. pressure.

β -Ethoxy- α -alanine, $OEt \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$, may be obtained as an intermediate product in the synthesis of serine just described and melts and decomposes at 256° (corr.). Its aqueous solution has a sweet taste, reacts faintly acid towards litmus, and assumes a deep blue tint when boiled with copper oxide. It is sparingly soluble in water and separates from 90 per cent. alcohol in needles. Its *copper* salt is described. When heated with concentrated hydrochloric acid, it is converted into serine.

β-Ethoxy-α-phenylureidopropionic acid,



prepared by the addition of phenylcarbimide to a solution of the ethoxyalanine in sodium hydroxide, separates from water in hexagonal plates and melts at 167—168° (corr.).

Ethoxyacetaldehydesemicarbazone, $\text{OEt} \cdot \text{CH}_2 \cdot \text{CH} : \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, prepared by the addition of semicarbazide hydrochloride to ethoxyacetaldehyde ammonia (m. p. 79—81°), separates from water in rhombohedra and melts at 85—86°.

A. McK.

Resolution of Racemic Serine into the Optically Active Components. EMIL FISCHER and WALTER A. JACOBS (*Ber.*, 1906, 39, 2942—2950).—*p*-Nitrobenzoyl-*dl*-serine, prepared by the gradual addition of *p*-nitrobenzoyl chloride and potassium hydroxide to serine in the cold, crystallises from water in light yellow, thin needles, which sinter at 184° (corr.) and melt and decompose to a brown liquid at 206—207° (corr.). After heating with quinine in alcohol, the quinine salt of the *d*-compound separates on cooling and on hydrolysis yields *p*-nitrobenzoyl-*d*-serine, crystallising in glistening, faintly yellow plates which sinter at 171° (corr.) and melt at 189.5° (corr.). It has $[\alpha]_D - 43.74^\circ$ at 20°. *d*-Serine, obtained from the foregoing on heating with hydrogen bromide, crystallises in large, colourless prisms or hexagonal plates which, on heating, become brown at 211° (corr.) and decompose about 228° (corr.). It has $[\alpha]_D + 6.87^\circ$ at 20° in water and -14.32° in *N*-hydrochloric acid and is approximately twice as soluble in water as racemic serine. The quinine salt of the *l*-compound is obtained from the mother liquors: to purify it, it is converted into the *brucine* salt, which crystallises in yellow prisms aggregated in rays. *p*-Nitrobenzoyl-*l*-serine is in every way similar to the *d*-compound, but has $[\alpha]_D + 43.56^\circ$ at 20°. Similarly, *l*-serine has $[\alpha]_D - 6.83^\circ$ at 20° in water and $+14.45^\circ$ in *N*-hydrochloric acid. *d*-Serine has a definitely sweet taste; that of *l*-serine is less, although still appreciably sweet. *l*-Serine methyl ester was obtained as a colourless, strongly alkaline syrup; the *hydrochloride* consists of colourless four- or eight-sided microscopic plates decomposing at 167° (corr.). *l*-Serine *anhydride* forms slender, colourless needles melting and decomposing at 247° (corr.); it has $[\alpha]_D - 67.46^\circ$ at 20°, and is identical with a product derived from silk fibroin. *l*-Serine is therefore regarded as the natural product.

The authors have also resolved *isoserine* and *diaminopropionic acid*. *Benzoylisoserine* has $[\alpha]_D + 10.45^\circ$ at 20°, whilst the isomeric *dibenzoyl-diaminopropionic acids* show $[\alpha]_D - 35.76^\circ$ and $+35.9^\circ$ at 20° respectively.

E. F. A.

Behaviour of Racemic Amino-acids towards Yeast. New Biological Method for resolving them. FELIX EHRLICH (*Zeit. Ver. deut. Zuckerind.*, 1906, 608, 840—860).—Racemic amino-acids are readily attacked by yeast in solutions containing a large proportion of sucrose. The yeast should be poor in nitrogen and should be used in large excess, in order that the destruction of one of the component amino-acids may be complete. Any ordinary clean baker's yeast is

suitable, pure cultures of the pressed yeasts of Classes II and XII giving especially good results. These yeasts can now be procured very constant in composition, the dry matter they contain amounting to about 25 and the nitrogen to about 2 per cent.

Ten grams of the racemic amino-acid and from 200 to 300 grams of sucrose are dissolved in 2 to 3 litres of water contained in a capacious flask, and the solution, which need not be sterilised, mixed with a quantity of pressed yeast varying, for different amino-acids, from 50 to 150 grams. The flask is closed by means of a sulphuric acid seal and is vigorously shaken for some time. The fermentation is allowed to proceed at the ordinary temperature, since, if higher temperatures are employed, the autolytic activity of the yeast becomes greater, and an increased amount of the yeast-substance is thus introduced into the solution. When the liquid no longer reduces Fehling's solution or gives the naphthol reaction, the fermentation is complete; this is generally found to be the case after thirty-six to forty-eight hours, whilst in some cases twenty-four hours are sufficient. The clear liquid is syphoned off and the residual yeast placed on a large filter and washed with a little water. The whole of the solution is then mixed with a little alumina cream or kieselguhr and filtered, the clear liquid thus obtained giving no biuret reaction and only a faint Millon's reaction. The solution is boiled to a volume of 100—200 c.c., filtered, if necessary, after the addition of animal charcoal, and evaporated on the water-bath to a thin syrup. While the latter is cooling, crystallisation is started by scratching the dish with a glass rod.

If the specific rotation of the product indicates the presence of racemic compound, a second fermentation should be carried out in the same way as the first.

From the compounds examined by the author, namely, racemic alanine, leucine, and α -aminoisovaleric acid, *l*-alanine, *d*-leucine, and *l*- α -aminoisovaleric acid were obtained in a pure state in yields amounting respectively to 65, 76, and 67 per cent. of the theoretical quantities. In all cases both optical isomerides are attacked by the yeast, but, as a rule, one far more rapidly than the other.

In hydrochloric acid solution, *d*-leucine has $[\alpha]_D -15.4^\circ$ at 20° (compare Fischer and Warburg, this vol., i, 72).

When submitted to the action of yeast in the manner described, synthetical α -amino- α -methylbutyric acid yields a levorotatory compound, and, with a mixture of *d*-isoleucine and *d*-alloisoleucine, obtained either synthetically from *d*-amyl alcohol or by the action of barium hydroxide solution on natural *d*-isoleucine, the latter gives up its nitrogen to the yeast and is converted into *d*-amyl alcohol, whilst the *d*-alloisoleucine is not appreciably attacked.

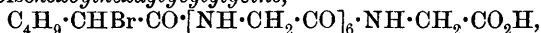
T. H. P.

Synthesis of Polypeptides. XV. EMIL FISCHER (*Ber.*, 1906, 39, 2893—2931).— α -Bromoisohexoyltetraglycylglycyl chloride is prepared from bromoisohexoyltetraglycylglycine by the action of acetyl chloride and phosphorus pentachloride in the apparatus previously described (*Abstr.*, 1905, i, 863). The glycine must be specially prepared for chlorination by solution in cold alkali hydroxide and slow precipitation with hydrochloric acid and subsequent drying in a vacuum;

if crystallised from water or alcohol, the carboxyl group of the polypeptide resists all attempts at chlorination.

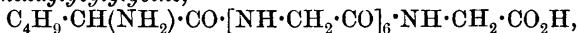
α-Bromoisohexoyl-pentaglycylglycyl chloride and *-hexaglycylglycyl chloride* are obtained as colourless solids in a similar manner.

α-Bromoisohexoylhexaglycylglycine,



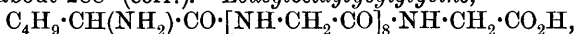
is prepared by condensation of triglycylglycine with *α-bromoisohexoyl-diglycylglycine chloride* in presence of sodium hydroxide, special experimental precautions being necessary to ensure success; it is obtained as a loose, colourless powder which, when quickly heated, turns yellow at about 245° (corr.) and melts and decomposes between 256° and 259° (corr.).

Leucylhexaglycylglycine,

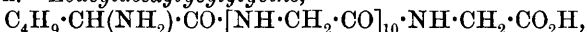


obtained by the action of liquid ammonia on the foregoing, is obtained as a microcrystalline, colourless powder with H₂O which, when rapidly heated, becomes yellow at about 200° and darkens and finally decomposes between 280° and 290°. It dissolves in hot hydrochloric acid, forming a sparingly soluble *hydrochloride*, and shows a marked biuret coloration.

α-Bromoisohexyloctaglycylglycine is prepared by coupling pentaglycylglycine with *α-bromoisohexoyldiglycylglycyl chloride* in presence of alkali; it turns yellow between 244° and 255° (corr.) and finally decomposes at about 288° (corr.). *Leucyloctaglycylglycine*,



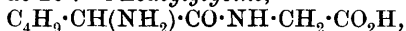
crystallises with H₂O, the dry substance being hygroscopic; it colours at 255° (corr.) and becomes black at 290° (corr.). *α-Bromoisohexoyl-decaglycylglycine* turns yellow at 230°, becomes brown above this, and black at about 293° (corr.); the alkaline solution gives a biuret coloration. *Leucyldecaglycylglycine*,



is a colourless, amorphous powder without a melting point; it shows a strong biuret coloration, is easily soluble in cold fuming hydrochloric acid, the *hydrochloride* being precipitated on dilution; the solution in dilute ammonia gives a dense precipitate with ammonium sulphate, and in this respect strongly resembles the natural proteids.

Active *α-bromoisohexoyldiglycylglycine*, prepared by condensation of diglycylglycine with *α-bromoisohexoyl chloride* from *d-leucine*, sinters at 163° (corr.) and melts at 168—169° (corr.) to a yellow liquid. In normal alkali it has $[\alpha]_D + 31.98^\circ$ at 20°. *l-Leucyldiglycylglycine*, $\text{C}_4\text{H}_9\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot[\text{NH}\cdot\text{CH}_2\cdot\text{CO}]_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, prepared by the action of aqueous ammonia on the preceding compound, forms stellar aggregates of glistening, prismatic crystals which, when quickly heated, become yellow at 220° (corr.) and melt at 230—232° (corr.), partially decomposing to a reddish-brown liquid. It has in aqueous solution $[\alpha]_D + 45.85^\circ$ at 20° and gives a marked biuret coloration.

d-α-Bromoisohexoylglycine, prepared from *d-α-bromoisohexoic acid* and glycine, softens at 82° and melts at 85—86° (corr.). It crystallises in stellar aggregates of long needles from alcohol, in which solvent it has $[\alpha]_D + 62.0^\circ$ at 20°. *l-Leucylglycine*,



sinters at 235° and melts at 248° (corr.), being partially converted into anhydride; it crystallises in needles and is more soluble in water than the racemic form; it tastes somewhat bitter, forms a deep blue copper salt, and has $[\alpha]_D + 85.5^\circ$ at 20°.

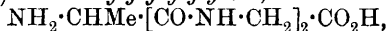
l-Leucylglycine anhydride, $C_4H_9 \cdot CH \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} > CH_2$, prepared under special precautions from the ester of the dipeptide, sinters at 245° and melts at 254—255° (corr.); it tastes bitter, reacts neutral, and shows $[\alpha]_D + 32.3^\circ$ at 20°. This anhydride is identical with a product obtained by Fischer and Abderhalden by the hydrolysis of elastin (this vol., i, 719).

d-α-Bromoisohexoyl-d-alanine crystallises in thin, long needles which soften at 96° and melt at 101—103° (corr.) and have $[\alpha]_D + 23.0^\circ$ at 20°.

l-Leucyl d-alanine, $C_4H_9 \cdot CH(NH_2) \cdot CO \cdot NH \cdot CHMe \cdot CO_2H$, forms flat, right-angled plates which taste bitter and melt at 257° (corr.); the copper salt crystallises in flat, blue prisms. The dipeptide dissolved in methyl alcohol gives $[\alpha]_D + 23.7^\circ$ at 20°. *α-Leucyl-d-alanine anhydride*, $C_4H_9 \cdot CH \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} > CHMe$, crystallises in long needles melting at 258° (corr.), tastes bitter, and has $[\alpha]_D - 29.0^\circ$ at 20°.

d-α-Bromoisohexoyl-l-leucine crystallises in microscopic, double pyramids, melting at 149° (corr.), and has $[\alpha]_D + 16.2^\circ$ at 20°. *l-Leucyl-l-leucine*, $C_4H_9 \cdot CH(NH_2) \cdot CO \cdot NH \cdot CH(C_4H_9) \cdot CO_2H$, crystallises from water or alcohol in long, pointed plates aggregated in rosettes which melt at 270° (corr.) and have $[\alpha]_D - 13.43^\circ$ at 20° in alkaline solution. It forms a crystalline *hydrochloride* and a blue *copper salt* separating in needles, and a characteristic *carbethoxy-l-leucyl-l-leucine*, of which the obliquely-cut plates melt at 149—150° (corr.) and are sparingly soluble even in hot water. *l-Leucine anhydride* (*l-leucineimide*), prepared from the methyl ester of the dipeptide, melts at 277° (corr.) and has $[\alpha]_D - 42.8^\circ$ at 20°.

l-Bromopropionylglycylglycine crystallises in colourless prisms melting at 172° (corr.). *l-Alanylglycylglycine*,



forms colourless, centimetre long needles, belonging to the monoclinic, hemimorphous system, with H_2O , which become yellow at 205° and melt and decompose at 245° (corr.). It does not show a biuret coloration, and gives a precipitate with phosphotungstic acid. The aqueous solution has $[\alpha]_D - 29.2^\circ$ at 20°. The *methyl ester* crystallises in colourless, glistening plates; it liquefies between 90° and 95°, and forms a *hydrochloride*, crystallising in bundles of needles, which melts at 178° (corr.). On heating at 100°, it is converted into the *ester* of the hexapeptide, a compound sintering at 175° and melting and decomposing at 185°, which gives a marked biuret coloration, and is hydrolysed by sodium hydroxide to *l-alanyldiglycyl-l-alanylglycylglycine*. This decomposes at 207° and has $[\alpha]_D + 13^\circ$ at 21°.

Triglycylglycine methyl ester, prepared by esterifying the tetrapeptide with methyl alcohol and hydrogen chloride, crystallises in microscopic, glistening needles or thin sheaves of prisms: it becomes yellow at 200° and decomposes at 240°. The *hydrochloride* forms microscopic

platelets which melt at 198—200°. It gives a brilliant biuret coloration, and does not condense on heating to 100°.

Methods are described for preparing formyl-*d*-, *l*-, and *dl*-leucine, and the measurements of their rhombic crystals given. Better methods of preparing *d*- α -bromoisohexoic acid, *d*- α -bromoisohexoyl chloride, and glycine anhydride are also described. E. F. A.

Dithiocarbamoglycollic Acid (Carboxymethyldithiourethane). B. HOLMBERG (*Ber.*, 1906, **39**, 3068—3069. Compare Abstr., 1905, i, 323).—*Dithiocarbamoglycollic acid (carboxymethyldithiourethane)*, $\text{NH}_2 \cdot \text{CS} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, is obtained when sulphuric acid is added to an aqueous solution of sodium chloroacetate and ammonium dithiocarbamate; it crystallises in needles or leaflets, darkens at 100°, and melts at 136—137°, yielding after a few minutes at the latter temperature the *anhydride*, $\text{S} \begin{array}{c} \text{CS}-\text{NH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CO} \end{array}$, which crystallises in large, yellow leaflets, melts and decomposes at 168—169°, and is also obtained by acidifying the mixture of sodium chloroacetate and ammonium dithiocarbamate with acetic acid, or in accordance with the equation $\text{CH}_2\text{SH} \cdot \text{CO}_2\text{H} + \text{CS}(\text{NH}_2)_2 = \text{C}_3\text{H}_3\text{ONS}_2 + \text{NH}_3 + \text{H}_2\text{O}$. C. S.

A New Group of Nitrogenous Carbohydrates. TH. R. OFFER (*Beitr. chem. Physiol. Path.*, 1906, **8**, 399—405. Compare Fränkel, Abstr., 1899, i, 396; Fränkel and Kelly, *ibid.*, 1902, i, 479).—A nitrogenous carbohydrate, which gives the pentose reactions, but reduces Fehling's solution after hydrolysis, has been isolated from horse's liver by extraction with alcohol after other substances had been removed by repeated extraction with acetone. Better yields are obtained by extracting the liver with hot water. After concentration of the clear extract, removal of proteids and glycogen, and further concentration and addition of methyl alcohol, a precipitate was obtained, which, after purification, was converted into its *copper* derivative, $\text{C}_{10}\text{H}_{16}\text{O}_7\text{N}_2(\text{CuO})_2$. The corresponding carbohydrate is probably a dipentosamine, $2(\text{C}_5\text{H}_7\text{O}_3 \cdot \text{NH}_2) + \text{H}_2\text{O}$.

From the alcoholic filtrate, a *barium* compound, $\text{C}_{14}\text{H}_{22}\text{O}_9\text{N}_2\text{Ba}$, has been obtained; this corresponds with a *diacetylated* dipentosamine, $\text{C}_{10}\text{H}_{18}\text{O}_7\text{N}_2\text{Ac}_2$. The barium compound is readily soluble in water or alcohol, but insoluble in ether or methyl alcohol. It does not reduce Fehling's solution until boiled with hydrochloric acid, and gives the characteristic pentose reactions only after prolonged boiling.

J. J. S.

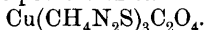
Chloro-derivatives of Diacetamide. HERMANN FINGER (*J. pr. Chem.*, 1906, [ii], **74**, 153).—*Hexachlorodiacetamide*, $\text{NH}(\text{CO} \cdot \text{CCl}_3)_2$, prepared by heating trichloroacetonitrile with trichloroacetic acid in a sealed tube at 180—190°, crystallises from light petroleum, melts at 81°, and is decomposed by alcohol, forming ethyl trichloroacetate and trichloroacetamide, or by ammonia, forming 2 mols. of trichloroacetamide, or by prolonged heating at 120—140°, yielding trichloroacetonitrile, trichloroacetamide, and hexachloroacetic anhydride. G. Y.

Action of Sodium Hypobromite on some Amino-compounds. J. STUHETZ (*Monatsh.*, 1906, 27, 601—605).—The action of sodium hypobromite on carbamide in aqueous solutions of different concentrations at the ordinary temperature and pressure leads to the evolution of 29·3—44·4 per cent. of nitrogen; the theoretical percentage, 46·6, was not evolved in any experiment.

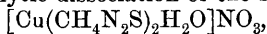
Glycine, alanine, leucine, glutamic acid, tyrosine, lysine, and histidine yield only very small quantities of nitrogen when treated with sodium hypobromite solution, whilst under the same conditions arginine evolves about 1/3 of its nitrogen. G. Y.

Salts of Cuprothiocarbamides. VOLKMAR KOHLSCHÜTTER and C. BRITTLEBANK (*Annalen*, 1906, 349, 232—268. Compare Rathke, *Abstr.*, 1884, 1017; Rosenheim and Loewenstamm, *Abstr.*, 1903, i, 325; Kohlschütter, *ibid.*, 468).—The greater part of this work has been published previously. The authors agree with Rosenheim and Stadler (this vol., i, 407) that the complex salts formed by thiocarbamide with cuprous chloride have the formulæ $\text{Cu}(\text{CH}_4\text{N}_2\text{S})\text{Cl}_2$, $\text{Cu}(\text{C}_6\text{H}_4\text{N}_2\text{S})_2\text{Cl}$, and $\text{Cu}(\text{CH}_4\text{N}_2\text{S})_3\text{Cl}$, the last on hydrolysis yielding the salt $[\text{Cu}(\text{CH}_4\text{N}_2\text{S})_2\text{H}_2\text{O}]\text{Cl}$.

The complex compound, $\text{Cu}(\text{CH}_4\text{N}_2\text{S})_3\text{Cl}$, is to be regarded as a salt of the univalent cation, $[\text{Cu}(\text{CH}_4\text{N}_2\text{S})_3]^+$, as on electrolysis with a current density of 0·02 ampere, the cathode vessel contains finally copper and thiocarbamide in the proportion 1:3·01; the abnormal conductivity results obtained with this salt are discussed and found to be in agreement with Kohlschütter's conclusions (*loc. cit.*). Contrary to Kohlschütter's statement, the oxalate formed on addition of oxalic acid to the chloride has the formula $\text{Cu}(\text{CH}_4\text{N}_2\text{S})_3\text{C}_2\text{HO}_4\cdot\text{H}_2\text{O}$, whilst that formed by addition of potassium oxalate has the formula

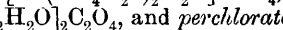


The salt $\text{Cu}(\text{CH}_4\text{N}_2\text{S})_3\text{NO}_3\cdot 4[\text{Cu}(\text{CH}_4\text{N}_2\text{S})_2\text{H}_2\text{O}]\text{NO}_3$ crystallises in slender needles when dilute nitric acid is added to a saturated solution of the salt $\text{Cu}(\text{CH}_4\text{N}_2\text{S})_3\text{NO}_3\cdot [\text{Cu}(\text{CH}_4\text{N}_2\text{S})_2\text{H}_2\text{O}]\text{NO}_3$. The comparison of the degree of electrolytic dissociation of the salt

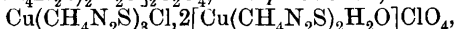


$\alpha = 0\cdot39$ with $v = 51\cdot3$, with the molecular conductivity, $\alpha = 0\cdot86$ with $v = 32$, shows that the part of the salt which is not electrolytically dissociated consists of polymeric molecules, and the solid salt is an association of several molecules of the above formula. The *sulphate*,

$[\text{Cu}(\text{CH}_4\text{N}_2\text{S})_3][\text{Cu}(\text{CH}_4\text{N}_2\text{S})_2\text{H}_2\text{O}]\text{SO}_4\cdot\text{H}_2\text{O}$, *hydrogen sulphate*,



oxalate, $[\text{Cu}(\text{CH}_4\text{N}_2\text{S})_2\text{H}_2\text{O}]_2\text{C}_2\text{O}_4$, and *perchlorate*,



are described.

The solubility of thiocarbamide in water increases on addition of cuprothiocarbamide chloride in proportion to the amount of the chloride added; similarly, the solubility of the chloride in water is increased by the presence of thiocarbamide, showing that a further addition of thiocarbamide to the cuprotrithiocarbamide takes place, which is in agreement with the results of the cryoscopic mol. weight determination.

Cuprodithiocarbamide chloride, $\text{Cu}(\text{CH}_4\text{N}_2\text{S})_2\text{Cl}$, formed by the action of potassium chloride on cuproaquodithiocarbamide nitrate, is a salt of the type of triaminocobalt nitrite, and is only very slightly dissociated.

The bearing of the behaviour of cuprodithiocarbamide chloride on the theory of the influence of the anion on the formation of complex cations is discussed.

Cuprothiocarbamide chloride, $\text{Cu}(\text{CH}_4\text{N}_2\text{S})\text{Cl}$, which occurs in two modifications, resembles cuprous chloride in its behaviour, dissolving in concentrated hydrochloric acid and, although less readily, in saturated sodium chloride solution; the solution in hydrochloric acid absorbs carbon monoxide. On electrolysis of the cupro-chloride in hydrochloric acid solution, the amount of thiocarbamide at the cathode diminishes in consequence of the wandering of anions containing thiocarbamide.

G. Y.

***iso*Butylhydantoic Acid and Detection of Small Quantities of Leucine.** FRITZ LIPPICH (*Ber.*, 1906, 39, 2953—2956).—Baumann and Hoppe-Seyler formerly observed that hydantoic acid was produced when a solution of glycine and carbamide was boiled with baryta water until the evolution of ammonia ceased. Similarly, Pinner and Spilker (*Abstr.*, 1889, 704) prepared *isobutyl*hydantoin from *isovaleraldehyde* hydrocyanide and carbamide, and thence obtained the *isobutyl*hydantoic acid corresponding with leucine by boiling with baryta water. It is probable that the reaction (the formation of hydantoic acids) is general for all the α -aminocarboxylic acids, and a preliminary experiment with aminovaleric acid has confirmed this supposition. The reaction may be used to detect small quantities of leucine in a mixture of other amino-acids. For example, a mixture of 1 gram of leucine, 0.5 gram of glycine, and 0.5 gram of tyrosine was boiled with carbamide and baryta water in moderate excess until the evolution of ammonia had ceased, the excess of barium was removed by carbon dioxide, and the filtrate cautiously acidified with acetic acid. The crystalline precipitate thus obtained was recrystallised from 50 per cent. alcohol, when the substance separated in aggregates of well-defined, colourless needles melting at 205° . The properties of this substance show that it is identical with Pinner and Spilker's *isobutyl*hydantoic acid. On account of the sparing solubility of the free *isobutyl*hydantoic acid and the great solubility of its crystallisable barium salt, this reaction may be generally applied to the detection of leucine, and as little as 0.01 gram of the pure amino-acid may be distinguished in this way.

G. T. M.

Specific Rotation of Glutamine. ERNST SCHULZE (*Ber.*, 1906, 39, 2932—2933. Compare *Abstr.*, 1885, 759).—Seven preparations of glutamine from various vegetable sources were found to have $[\alpha]_D$ between $+1.9^\circ$ and $+9.5^\circ$, the differences being probably due to the preparations containing the two stereoisomerides in varying proportions.

E. F. A.

Complex Compounds of Organic Imides. Succinimide Nickel Derivatives. LEO TSCHUGAEFF (*Ber.*, 1906, **39**, 3190—3201. Compare Abstr., 1904, i, 478; 1905, i, 865).—The succinimide nickel group, $(\text{Su})_2\text{Ni}$ [$\text{Su} = \text{C}_2\text{H}_4(\text{CO})_2\text{N}$], combines with aliphatic monoamines to form a series of compounds, $(\text{Su})_2\text{Ni}, 2a$ [$a = \text{an amine}$], which resemble in general character the copper compounds already described. The compounds in question are prepared according to two methods: (1) Interaction of nickel salts and amines in presence of a slight excess of succinimide, the action, which is conducted in alcoholic solution, being in accordance with the scheme $\text{NiX}_2 + 2\text{SuH} + 4a = \text{Ni}(\text{Su})_2, 2a + 2a, \text{HCl}$. (2) Action of amines on nickel succinimide octahydrate, the reaction taking place either at the ordinary temperature or on gentle warming in the presence of a little alcohol, thus: $(\text{Su})_2\text{Ni}, 8\text{H}_2\text{O} + 2a = (\text{Su})_2\text{Ni}, 2a + 8\text{H}_2\text{O}$.

The compounds $(\text{Su})_2\text{Ni}, 2a$ form yellow needles, and undergo no change when kept under diminished pressure over sulphuric acid. They are also moderately stable towards heat, and begin to decompose above 200° . Solutions in water and in alcohol are bluish-green and unstable. Aqueous solutions readily undergo hydrolytic dissociation, with separation of nickelous hydroxide. The compounds are readily decomposed by acids, thus: $(\text{Su})_2\text{Ni}, 2a + 4\text{HX} = 2\text{SuH} + 2a\text{HX} + \text{NiX}_2$. The following compounds are described: *methylamine* compound, $(\text{Su})_2\text{Ni}, 2\text{Me}\cdot\text{NH}_2$; *propylamine* compound, $(\text{Su})_2\text{Ni}, 2\text{Pr}\cdot\text{NH}_2$; *isobutylamine* compound, $(\text{Su})_2\text{Ni}, 2\text{C}_4\text{H}_9\cdot\text{NH}_2$; *allylamine* compound, $(\text{Su})_2\text{Ni}, 2\text{C}_3\text{H}_5\cdot\text{NH}_2$; *camphylamine* compound, $(\text{Su})_2\text{Ni}, 2\text{C}_{10}\text{H}_{17}\cdot\text{NH}_2, 2\text{H}_2\text{O}$;

the latter forms lilac needles.

The only compound obtained from a secondary amine was a yellow, crystalline, very unstable compound from dimethylamine and the octahydrate, whilst tertiary amines do not form double compounds with succinimide.

When an excess of succinimide is added to a concentrated solution of nickel chloride or of nickel acetate, and trimethylamine is then added to the warm solution, the *octahydrate*, $(\text{Su})_2\text{Ni}, 8\text{H}_2\text{O}$, separates as bright blue needles.

Triethylenediamine nickel succinimide, $\text{C}_{14}\text{H}_{32}\text{O}_4\text{N}_8\text{Ni}, 2\text{H}_2\text{O}$, prepared by the action of ethylenediamine on the octahydrate, crystallises in reddish-violet prisms. It decomposes at about 200° . Its aqueous solutions are reddish-violet.

Propylenediamine and butylenediamine also react with the octahydrate. The compound $\text{C}_8\text{H}_{20}\text{N}_6\text{S}_2\text{Ni}$ is formed when potassium thiocyanate is added to the solution obtained by the addition of trimethylenediamine to the octahydrate; it crystallises in lilac needles or prisms.

The action of tetramethylenediamine and pentamethylenediamine respectively on the octahydrate was also studied, but well-defined compounds were not obtained.

A. McK.

Cobalt Dioximines. LEO TSCHUGAEFF (*Ber.*, 1906, **39**, 2692—2702. Compare Abstr., 1904, i, 478; 1905, i, 743, 865).—The ammine derivatives of the dioximines can be formulated in accordance with Werner's

theory, the complex D_2H_2 (where $D = \begin{smallmatrix} R \cdot C : NO \cdot \\ | \\ R \cdot C : NO \cdot \end{smallmatrix}$) occupying four positions in the metallic complex. Moreover, the ammonia can be replaced by methylamine, ethylamine, or pyridine.

Diamminedimethylglyoximinecobalt chloride, $[Co(NH_3)_2D_2H_2]Cl \cdot 5H_2O$, is obtained (1) by heating dimethylglyoxime, chloropentamminecobalt chloride (purpureochloride), and a solution of ammonium acetate on the water-bath; (2) in a similar manner from hexamminecobalt chloride (luteochloride), dimethylglyoxime, and excess of ammonium acetate; (3) from carbonatotetramminecobalt sulphate as in (2), excess of potassium or ammonium chloride being added to precipitate the chloride; (4) by passing air through a concentrated solution of cobaltous chloride, dimethylglyoxime, and excess of 10 per cent. ammonium hydroxide, ammonium chloride being finally added after the solution has been evaporated to a small bulk.

Chloroamminedimethylglyoximinecobalt, $[CoCl(NH_3)D_2H_2]$, is obtained when the first-mentioned method of preparation is carried out in the presence of acetic acid; it crystallises in dark brown needles or prisms, is stable to acids or alkalis, does not contain ionisable chlorine, and consequently does not possess electrical conductivity. Concentrated sulphuric acid dissolves the substance, forming a rose-red solution, which evolves hydrogen chloride only when heated strongly. The substance is converted into the preceding chloride by treatment with ammonium hydroxide.

Nitritoamminedimethylglyoximinecobalt, $[Co(NO_2)(NH_3)D_2H_2]$, obtained from xantho- or isoxantho-cobalt chloride, separates from hot water in small, yellowish-brown prisms. The nitrite group is not ionisable.

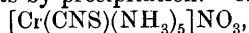
Diethylaminedimethylglyoximinecobalt chloride, $[Co(NH_2Et)_2D_2H_2]Cl$, results when air is passed for four to five hours through a solution of cobalt chloride, dimethylglyoxime, and ethylamine. It separates from hot water in small, brownish-yellow prisms or plates, and is very soluble in water. Potassium iodide or nitrate or sodium chlorate precipitate the corresponding sparingly soluble salts. The *iodide* separates from 30—40 per cent. alcohol in golden-yellow needles; the *nitrate* crystallises from hot water. The *base*, $[Co(NH_2Et)_2D_2H_2] \cdot OH$, obtained from the chloride and silver oxide, is only stable in solution; it has an alkaline reaction, absorbs carbon dioxide from the atmosphere, precipitates the hydroxides of the heavy metals, and with acids yields the corresponding salts. The solution has a yellowish-brown colour and does not smell of ethylamine.

Dipyridinedimethylglyoximinecobalt chloride, $[Co(C_5NH_5)_2D_2H_2]Cl$, obtained in 50 per cent. alcoholic solution in a similar manner to the ethylamine compound, separates in large, dark brown crystals. When it is dissolved in warm water and treated with a slight excess of potassium hydroxide, the *anhydro-base*, $[Co(C_5NH_5)_2D_2H_2]$, is obtained quantitatively as a dark brown, crystalline precipitate. The *nitrate*, $[Co(C_5NH_5)_2D_2H_2]NO_3$, obtained by dissolving the anhydro-base in dilute nitric acid, forms brown, nacreous leaflets, is electrolytically

dissociated in aqueous solution, and yields, with potassium iodide or thiocyanate, precipitates of the corresponding salts. C. S.

Thiocyanoamminechromium Salts. VI. Chromium Salts.

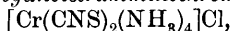
ALFRED WERNER and J. VON HALBAN (*Ber.*, 1906, **39**, 2668—2673. Compare this vol., ii, 452).—*Thiocyanopentamminechromium thiocyanate*, $[\text{Cr}(\text{CNS})(\text{NH}_3)_5] \cdot \text{CNS}$, is obtained when chloropentamminechromium chloride (compare Christensen, *Abstr.*, 1893, ii, 469) is boiled with an excess of a concentrated acetic acid solution of potassium thiocyanate; it separates in aggregates of orange or reddish-brown leaflets, is easily soluble in hot water, has not been obtained pure, and yields the following salts by precipitation. The *nitrate*,



separates from dilute acetic acid in orange-yellow crystals; the *dichromate*, $[\text{Cr}(\text{CNS})(\text{NH}_3)_5]_2 \text{Cr}_2 \text{O}_7$, crystallises in bronze-coloured needles; the *chloride*, $[\text{Cr}(\text{CNS})(\text{NH}_3)_5] \text{Cl}_2$, is very stable to concentrated hydrochloric acid; the *bromide*, $[\text{Cr}(\text{CNS})(\text{NH}_3)_5] \text{Br}_2$, crystallises in deep orange crystals.

Nitratopentamminechromium nitrate, $[\text{Cr}(\text{NO}_3)(\text{NH}_3)_5](\text{NO}_3)_2$, is obtained from concentrated nitric acid, and the preceding nitrate or the aquopentamminechromium base derived from the chloropentamminechromium chloride; it is sparingly soluble in cold water, and at 30—40° the colour of the solution changes from red to violet, and the nitrate-salt cannot be recovered. The *iodide*, $[\text{Cr}(\text{NO}_3)(\text{NH}_3)_5] \text{I}_2$, is obtained from the nitrate and potassium iodide.

When thiocyanopentamminechromium thiocyanate is heated at 130—140°, until the evolution of ammonia ceases, a mixture is obtained from which *dithiocyanotetramminechromium chloride*,



and *trithiocyanotriamminechromium*, $\text{Cr}(\text{CNS})_3(\text{NH}_3)_3$, have been isolated. The latter is insoluble in cold water, alcohol, ether, or chloroform, but dissolves in piperidine, quinoline, benzylamine, acetonitrile, or acetone, being reprecipitated by the addition of ether. C. S.

Insoluble Chromicyanides. FREDERICK VAN DYKE CRUSER and EDMUND H. MILLER (*J. Amer. Chem. Soc.*, 1906, **28**, 1132—1151).—Potassium chromicyanide, $\text{K}_3\text{Cr}(\text{CN})_6$, was prepared by a modification of Christensen's method (*Abstr.*, 1885, 737). The following salts were obtained as insoluble precipitates by adding solution of potassium chromicyanide to solutions of metallic salts.

Cadmium chromicyanide, $\text{Cd}_3\text{Cr}_2(\text{CN})_{12}$, forms a white precipitate with a slightly green tinge. *Cobalt chromicyanide*, $\text{Co}_3\text{Cr}_2(\text{CN})_{12}$, is obtained as a light rose-coloured precipitate which becomes yellowish-brown on drying. *Cuprous chromicyanide*, $\text{Cu}_3\text{Cr}(\text{CN})_6$, forms an orange-yellow precipitate. *Cupric chromicyanide*, $\text{Cu}_3\text{Cr}_2(\text{CN})_{12}$, is blue when first precipitated, but gradually becomes green, and when dry is reddish-purple. *Ferrous chromicyanide*, $\text{Fe}_3\text{Cr}_2(\text{CN})_{12}$, is obtained as a brick-red, granular precipitate, which, on drying, becomes dark green. *Manganous chromicyanide*, $\text{Mn}_3\text{Cr}_2(\text{CN})_{12}$, forms a greenish-white, crystalline precipitate, and when dry is of a light brown colour. *Nickel chromicyanide*, $\text{Ni}_3\text{Cr}_2(\text{CN})_{12}$, forms a light greenish-blue precipitate which becomes black on drying. *Silver*

chromicyanide, $\text{Ag}_3\text{Cr}(\text{CN})_6$, is obtained as an orange-yellow precipitate, and when dry is rose-red in colour. *Zinc chromicyanide*, $\text{Zn}_3\text{Cr}_2(\text{CN})_{12}$, forms a yellowish-white, crystalline precipitate which becomes straw-coloured on drying.

On adding potassium chromicyanide solution to mercurous nitrate solution, a yellowish-white precipitate is produced, which rapidly darkens and finally becomes grey. It is probable that the original precipitate consists of mercurous chromicyanide, which decomposes with formation of mercurous cyanide, the latter becoming converted into mercuric cyanide and mercury.

The action of various reagents, such as the mineral acids, alkali hydroxides, and sodium peroxide, on these insoluble chromicyanides is described.

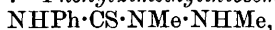
Solutions of lead acetate and nitrate of *N*/10 strength do not yield precipitates with *N*/10 potassium chromicyanide. A list is given of a large number of other salts which also fail to give a precipitate with this reagent. E. G.

Reactions at Low Temperatures. I. Cyanides. WALTER PETERS (*Ber.*, 1906, **39**, 2782—2784).—The compounds described were prepared by dissolving separately the base and hydrogen cyanide in absolute ether, cooling to -70° , and then mixing.

Diethylammonium cyanide is colourless, soluble in alcohol, and decomposes between -20° and -30° . *Triethylammonium cyanide* crystallises in needles and decomposes between -40° and -50° . *Dimethylhydrazinium cyanide* also crystallises in needles, decomposing between -6° and -10° . *Pentamethylenediaminium cyanide* soon becomes sticky, and decomposes from -40° to -50° . *Piperidinium cyanide* decomposes from -25° to -35° , whilst *coninium cyanide* decomposes at about -40° to -50° . E. F. A.

***s*-Dimethylhydrazine.** LUDWIG KNORR and A. KÖHLER (*Ber.*, 1906, **39**, 3257—3265).—When 1-methylpyrazole methiodide (obtained quantitatively from pyrazole, methyl alcohol and methyl iodide) is heated with a concentrated solution of potassium hydroxide, formic acid and a basic oil are produced; the latter has not been thoroughly examined, but from it *s*-dimethylhydrazine has been isolated. It boils at 81° under 747 mm. pressure, has a sp. gr. 0.8274 and n_D 1.4209 at 20° (compare Harries and Klamt, *Abstr.*, 1895, i, 262). The *acid hydrochloride*, *acid sulphate*, and *acid oxalate*, and the *picrate* and *picrolonate*, are described.

Dimethylsemicarbazide, $\text{NH}_2\cdot\text{CO}\cdot\text{NMe}\cdot\text{NHMe}$, obtained from *s*-dimethylhydrazine, hydrochloric acid, and potassium cyanate, melts at 116° . *s*-Dicarbanilyldimethylhydrazine, $\text{N}_2\text{Me}_2(\text{CO}\cdot\text{NHPh})_2$, obtained from phenylcarbimide and the base in ethereal solution, melts and decomposes at 288° . *Phenyldimethylthiosemicarbazide*,

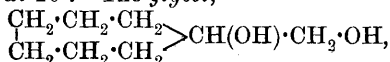


melts at 115° . *s*-Dibenzoilyldimethylhydrazine, $\text{NMeBz}\cdot\text{NMeBz}$, obtained by the Schotten-Baumann method, melts at 85° . *Dimethylpicrazide*, $\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{NMe}\cdot\text{NHMe}$, obtained from *s*-dimethylhydrazine and picryl chloride in alcoholic solution, melts at 141° . C. S.

Explanation of the Substitution of Aromatic Compounds.

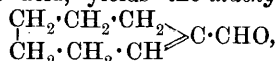
ARNOLD F. HOLLEMAN (*J. pr. Chem.*, 1906, [ii], 74, 157—160. Compare Abstr., 1903, i, 623).—An amplification of the author's criticisms of Flürscheim's theory of substitution in the aromatic series (Abstr., 1903, i, 79; 1905, i, 614; this vol., ii, 529). G. Y.

The Simplest Methylene Hydrocarbons of Various Ring Systems and their Conversion into Alicyclic Aldehydes. OTTO WALLACH [with H. KÖHLER] (*Chem. Centr.*, 1906, ii, 602; from *Nachr. k. Ges. Wiss. Göttingen*, 1906, 74—80. Compare this vol., i, 553).—*Methylenecycloheptane* boils at 138—140°, has a sp. gr. 0.824 at 20°, and $n_D = 1.4611$ at 20°. The *glycol*,



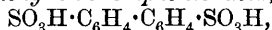
obtained from it melts at 50—51° and boils at 135—140°; on warming with dilute sulphuric acid, it yields suberanaldehyde, $\text{C}_8\text{H}_{14}\text{O}$, the semicarbazone of which melts at 153—154°.

When hydrochloric acid is removed from the nitrosochloride of methylenecycloheptane, a liquid oxime is obtained which, when warmed with dilute sulphuric acid, yields the *aldehyde*,



the *semicarbazone* of which melts at 203—204°. When oxidised by means of silver oxide, the aldehyde is converted into suberenecarboxylic acid, which melts at 50—51°. H. M. D.

Constitution of Griess' Benzinedisulphonic Acid. GUSTAV SCHULTZ and W. KOHLHAUS (*Ber.*, 1906, 39, 3341—3345. Compare Griess, Abstr., 1881, 428; Griess and Duisberg, Abstr., 1890, 57).—Griess' benzinedisulphonic acid is 4:4'-diaminodiphenyl-3:3'-disulphonic acid, as on elimination of the amino-groups by diazotisation and treatment of the product with copper powder in alcoholic solution it yields *diphenyl-3:3'-sulphonic acid*,



which on fusion with potassium hydroxide is converted into Haeussermann and Teichmann's 3:3'-dihydroxydiphenyl (Abstr., 1894, i, 598).

The 3:3'-disulphonic acid is obtained as a syrup; it is isolated in the form of its *potassium* salt, $\text{C}_{12}\text{H}_8\text{O}_6\text{S}_2\text{K}_2 \cdot 2\text{H}_2\text{O}$, which crystallises in almost colourless leaflets and is readily soluble in alcohol or water.

Diphenyl-3:3'-disulphonyl chloride, $\text{C}_{12}\text{H}_8(\text{SO}_2\text{Cl})_2$, crystallises from chloroform in colourless needles, and melts at 127.5—128°; the 3:3'-*disulphonamide*, $\text{C}_{12}\text{H}_8(\text{SO}_2\text{NH}_2)_2$, crystallises in stellate aggregates of microscopic needles and melts at 285°; the 3:3'-*disulphonanilide*, $\text{C}_{12}\text{H}_8(\text{SO}_2\text{NHPh})_2$, crystallises in glistening, prismatic, almost colourless prisms and melts at 181.5°. *Methyl diphenyl-3:3'-disulphonate*, $\text{C}_{12}\text{H}_8(\text{SO}_3\text{Me})_2$, crystallises in white needles and melts at 132.5°. 3:3'-Dihydroxydiphenyl crystallises in needles and gives a bluish-violet coloration with ferric chloride. The

dibenzoate, $C_{12}H_8(OBz)_2$, crystallises in white needles and melts at 92° . G. Y.

Benzylsulphinic Acid and Dibenzylsulphoxide. EMIL FROMM and JOSÉ DE SEIXAS PALMA (*Ber.*, 1906, **39**, 3308—3317. Compare Otto and Lueders, *Abstr.*, 1880, 811).—Dibenzylsulphone is formed always as an impurity in the preparation of benzylsulphinic acid.

In aqueous solution at the ordinary temperature, sodium benzylsulphonate undergoes slight decomposition, yielding small quantities of benzaldehyde; at higher temperatures, benzoic acid, stilbene, sulphur, and thionessal are formed. Benzylsulphinic acid, prepared by the action of hydrogen sulphide on lead benzylsulphonate, crystallises in needles, is unstable in aqueous solution, being readily hydrolysed to sulphur dioxide and benzaldehyde, and reduces iodine; when treated with methyl iodide and sodium hydroxide, it forms benzylmethylsulphone.

Dibenzylsulphoxide, $CH_2Ph \cdot SO \cdot SO \cdot CH_2Ph$, is formed by the decomposition of benzylsulphinic acid in aqueous solution. It crystallises in prisms, melts at 108° , is neutral, does not reduce iodine, and when treated with methyl iodide and potassium hydroxide yields benzylmethylsulphone; when boiled with benzyl chloride and sodium hydroxide, it forms dibenzylsulphone and dibenzylsulphoxide.

Benzylsulphonanilide, $CH_2Ph \cdot SO_2 \cdot NHPh$, crystallises in white needles melting at 103° ; the *p*-toluidide, $C_{14}H_{15}O_2NS$, forms white prisms melting at 113° ; the *o*-phenetide, $C_{15}H_{17}O_2NS$, crystallises in white prisms and melts at 85° .

Sodium and lead benzylsulphinates are formed by reduction of benzylsulphonyl chloride with zinc dust and alcohol; they decolorise iodine, but not indigotin, and when boiled with alkyl haloids form benzylalkylsulphones.

Benzylmethylsulphone, $CH_2Ph \cdot SO_2Me$, crystallises in long needles and melts at 127° .

Benzylethylsulphone, $CH_2Ph \cdot SO_2Et$, forms scales or needles and melts at 84° . G. Y.

Oxides of Hydrogen Sulphide. EMIL FROMM and JOSÉ DE SEIXAS PALMA (*Ber.*, 1906, **39**, 3317—3326).—When boiled with sodium hyposulphite and a trace of zinc dust in 30 per cent. aqueous sodium hydroxide, benzyl chloride yields dibenzylsulphone and sodium benzylsulphonate; the hyposulphite reacts therefore as a mixture of a sulphite and a sulfoxylate. The action of sodium hyposulphite on benzyl chloride in 50 per cent. aqueous sodium hydroxide at the ordinary temperature leads to the formation of sodium benzylsulphinate, which is identified by conversion into benzylmethylsulphone (compare preceding abstract).

Zinc dust reacts with sulphuryl chloride in ethereal solution, forming zinc chloride and *zinc sulfoxylate*, $ZnSO_2$, which is converted into dibenzylsulphone when heated with benzyl chloride and 10 per cent. sodium hydroxide; benzylsulphonic acid is not formed, as would be the case were the product of the sulphuryl chloride reaction zinc hypo-

sulphite. The syrupy product obtained on evaporating the ethereal solution of the sulphyxylate reduces indigotin.

Attempts were made to prepare sulphur hydrate, H_2SO , the hypothetical parent substance of the organic sulphyxides, which lies between hydrogen peroxide and hydrogen persulphide.

The action of thionyl chloride on zinc dust leads to the formation of zinc chloride, sulphur dioxide, and sulphur; a sulphyxide is not formed by treating the mixed products with benzyl chloride.

Benzyl disulphide, sulphide, and mercaptan are formed by the action of benzyl chloride on the product of the oxidation of sodium sulphide by hydrogen peroxide.

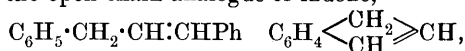
Sodium sulphide is oxidised to only a small extent by the hypochlorite yielding sodium sulphate.

The action of sulphur on potassium hydroxide and treatment of the product with benzyl chloride leads to the formation of thiobenzoic and benzoic acids together with a small amount of benzyl disulphide.

Thiobenzoic acid is oxidised to benzoyl disulphide by potassium ferri cyanide in alkaline solution. G. Y.

9-Ethylphenanthrene. ROBERT PSCHORR (*Ber.*, 1906, **39**, 3128—3129).—9-*Phenanthrylmethylcarbinol*, $\text{C}_{14}\text{H}_9\cdot\text{CHMe}\cdot\text{OH}$, resulting from acetaldehyde and 9-bromophenanthrene by the Grignard method, melts at 137° (corr.), and forms an *acetate*, $\text{C}_{19}\text{H}_{18}\text{O}_2$, which melts at 100° and boils at $230\text{--}235^\circ$ under 12 mm. pressure. By distillation with zinc dust, the carbinol yields 9-ethylphenanthrene, $\text{C}_{16}\text{H}_{14}$, which melts at $61\text{--}63^\circ$, forms a *picrate* melting at 124° , and by oxidation with chromic acid yields phenanthraquinone. C. S.

$\alpha\gamma$ -Diphenylpropylene. WALTER DIECKMANN and HERMANN KÄMMERER (*Ber.*, 1906, **39**, 3046—3051).— $\alpha\gamma$ -Diphenylpropylene may be regarded as the open chain analogue of indene,



and accordingly it has been studied with the view of ascertaining how far the capacity for condensation exhibited by indene, fluorene, and cyclopentadiene, and due to the neighbouring ethylene linkings present in these substances, would be recognisable in open chain compounds of similar constitution. The anticipation that the methylene group of $\alpha\gamma$ -diphenylpropylene would have the same reactivity as that in indene has not been confirmed; the results tend to show that the reactivity of the double linking is increased by the cyclic structure.

$\alpha\gamma$ -Diphenylpropylene may be prepared from benzylcinnamic acid, obtained by condensing benzaldehyde and dihydrocinnamic acid; this is heated at 100° with a saturated glacial acetic acid solution of hydrogen bromide, when β -bromodibenzylacetic acid is formed, which crystallises from glacial acetic acid in colourless, lustrous needles melting at $191\cdot5^\circ$. This acid is converted quantitatively into $\alpha\gamma$ -diphenylpropylene by warming with excess of aqueous sodium hydroxide. The hydrocarbon thus obtained, which boils at $178\text{--}179^\circ$ under 15 mm. pressure, is a colourless liquid with the fragrant odour of hyacinths; its molecular weight corresponds with

the formula $C_{15}H_{14}$. It is probably a stereoisomeride of the solid hydrocarbon (m. p. 57°) obtained by Francis (*Trans.*, 1899, **75**, 869), as the oily hydrocarbon gives a *dibromide* melting at 110° , whilst that derived from the solid hydrocarbon melts at 231° .

The hydrocarbon may be prepared also from $\alpha\gamma$ -diphenyl- α -propanol or from $\alpha\gamma$ -diphenyl- β -propanol by conversion into the crude chlorides, which are then heated with diethylaniline, or preferably with pyridine.

$\alpha\gamma$ -Diphenylpropylene does not condense with ethyl oxalate or diazo-compounds, benzaldehyde or cinnamaldehyde, and it does not develop any coloration with ferric chloride. It is not affected by ethyl nitrite and sodium in dry ethereal solution. When oxidised with permanganate, either in aqueous or acetone solution, it furnishes benzoic, phenylacetic, and benzoylformic acids, the last two being formed in relatively small proportions.

G. T. M.

Preparation of Triphenylmethane by the Action of Chloroform or Benzylidene Chloride on Magnesium Phenyl Bromide.

ALBERT REYCHLER (*Bull. Soc. chim.*, 1906, [iii], **35**, 737—740).—When chloroform, dissolved in ether, is added to magnesium phenyl bromide dissolved in ether, and the liquid is treated in the usual way, a yield of triphenylmethane equivalent to from 70—80 per cent. of the theoretical is obtained. When chloroform is replaced by benzylidene chloride in this reaction, some tetraphenylmethane is produced in addition to triphenylmethane.

Carbon tetrachloride reacts very violently with magnesium phenyl bromide. Benzenyl trichloride also reacts energetically, forming a crystalline precipitate which, submitted to the usual treatment, yields only a sticky product. Commercial methylene dichloride also reacts with magnesium phenyl bromide, yielding triphenylmethane, but this is probably entirely due to the chloroform present in the commercial article. Chloroform reacts with magnesium ethyl bromide, yielding a colourless precipitate.

T. A. H.

Triphenylmethyl. XIV. MOSES GOMBERG and LEE H. CONE (*Ber.*, 1906, **39**, 2957—2970. Compare this vol., i, 414).—The $\alpha\beta\beta\beta$ -Tetraphenylethane prepared by the authors' method was found to be identical in all respects with the product formerly obtained by Hanriot and Saint-Pierre (*Abstr.*, 1889, 882); the pure hydrocarbon may be distilled under reduced pressure, when it boils at 277 — 280° under 21 mm. pressure.

aaa-Triphenylpropane, formerly obtained as an oil, has now been caused to solidify by sowing with a crystal of the next homologue, triphenylbutane; after crystallisation from methyl alcohol, it melts at 51° .

It was also shown that the oily products obtained by E. and O. Fischer (*Annalen*, 1878, **194**, 259), and by Hanriot and Saint-Pierre (*loc. cit.*), contain crystallisable *aaa*-triphenylpropane.

aaa-Triphenylbutane, prepared by the interaction of magnesium propyl bromide and triphenylmethyl chloride, propylene and triphenylmethane being obtained as by-products, crystallises from methyl or ethyl alcohol in fine needles or in hexagonal plates; both forms melt at 79° , and the substance boils at 262 — 265° under 62 mm. pressure.

When *aaa*-triphenylethane is prepared by the interaction of triphenylmethyl chloride and magnesium methiodide, no gaseous olefine was evolved, as in the case of magnesium ethyl or propyl haloid, and the yield of the product was 70 per cent. of the calculated amount.

aaa-Triphenylisobutane, produced from magnesium isopropyl bromide and triphenylmethyl chloride, boils at 233—234° under 21 mm. pressure, and has not been solidified.

aaa-Triphenylisohexane, prepared from magnesium isoamyl bromide and triphenylmethyl chloride, is a viscid, pale yellow, highly refractive oil having an intense blue fluorescence.

The hydrocarbons of this series can all be nitrated with excess of fuming nitric acid until the number of entrant nitro-groups corresponds with the number of phenyl nuclei in the molecule, but in some cases the nitration must be repeated before this result is attained. All the nitrohydrocarbons, with the exception of trinitrotriphenylbutane, give the magenta reaction, and are therefore probably tri-*para*-derivatives. Two isomeric *tetranitro-as-tetraphenylethanes* were obtained, a more soluble substance present only in small quantities and melting at 258°, and the less soluble main product which melts at 269°.

Trinitro-aaa-triphenylpropane, obtained after repeated nitration of the hydrocarbon, crystallises from glacial acetic acid in pale yellow plates and melts at 194—195°.

Trinitro-aaa-triphenylbutane crystallises from glacial acetic acid and melts at 191—192°. *Trinitro-aaa-triphenylisobutane* melts at 262—263°. *Trinitro-aaa-triphenylisohexane* crystallises in prisms, melts at 207—208°, and, like the foregoing nitro-derivative, it dissolves sparingly in glacial acetic acid.

The compound from phenyldiphenylenechloromethane, described in the last communication as a hydrocarbon (this vol., i, 414), is now found to be *phenylfluorene peroxide*, $\text{C}_6\text{H}_4 > \text{CPh} \cdot \text{O} \cdot \text{O} \cdot \text{CPh} < \text{C}_6\text{H}_4$; this substance separates from benzene in transparent, tabular crystals containing $2\text{C}_6\text{H}_6$, which evolve the solvent on exposure to air and then melt at 193°. This peroxide may also be prepared by shaking a benzene solution of phenyldiphenylenechloromethane with 5 per cent. aqueous sodium peroxide containing some acetic acid. G. T. M.

Triphenylmethyl. XV. MOSES GOMBERG and LEE H. CONE (*Ber.*, 1906, 39, 3274—3297. Compare *Abstr.*, 1905, i, 641; Heintschel, *Abstr.*, 1903, i, 243; Jacobson, *Abstr.*, 1905, i, 186).—The present views as to the constitution of triphenylmethyl are (1) that it contains a tervalent carbon atom, (2) that it is hexaphenylethane, and (3) that it is a quinonic substance.

(2) This view can be no longer upheld, as tetraphenyl- and pentaphenylethane have been prepared and found to be stable substances.

(3) Heintschel's formula



does not explain why triphenylmethyl yields triphenylmethyl iodide

when treated with iodine. Jacobson's formula has been discussed previously (Abstr., 1905, i, 641).

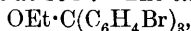
The following halogen substitution products of triphenylmethyl have been prepared by Friedel-Craft's synthesis or by Grignard's reaction (compare Gomberg, Abstr., 1904, i, 489).

p-Chlorotriphenylchloromethane, prepared from *p*-chlorobenzophenone and magnesium phenyl bromide, reacts with *p*-toluidine, forming *p*-chlorotriphenylmethyl-*p*-toluidine, $C_{26}H_{23}NCl$, melting at 131° . The *carbinol*, $OH \cdot CPh_2 \cdot C_6H_4Cl$, formed by hydrolysis of the chloride with sulphuric acid, crystallises with difficulty and melts at 85° . *p*-Bromotriphenylchloromethane, prepared from *p*-bromobenzophenone and magnesium phenyl bromide, melts at 114° . The *carbinol* crystallises slowly and melts at 74° . *p*-Iodotriphenylchloromethane, prepared from benzophenone dichloride, iodobenzene, and aluminium chloride, melts at 123° .

Di-p-chlorotriphenylchloromethane, $CPhCl(C_6H_4Cl)_2$, prepared from *p*-chlorobenzophenone and magnesium phenyl bromide and purified by means of its green, iridescent *ferrichloride*, $C_{19}H_{13}Cl_3 \cdot FeCl_3$, separates from light petroleum in opaque, crystalline aggregates and melts at 87° . The corresponding *di-p*-bromo-compound melts at 100° ; the *carbinol* crystallises from light petroleum in opaque masses and melts at 110° .

2:4':4''-Trichlorotriphenylchloromethane, $CCl(C_6H_4Cl)_3$, prepared together with a small quantity of tri-*p*-chlorotriphenylchloromethane, which is more soluble in light petroleum than is the 2:4':4''-compound, or by the action of carbon tetrachloride and aluminium chloride on chlorobenzene at $60-70^{\circ}$, or from magnesium *p*-chlorophenyl iodide and 2:4'-dichlorobenzophenone, forms large crystals and melts at 153° . The corresponding *carbinol*, $OH \cdot C(C_6H_4Cl)_3$, crystallises from light petroleum, melts at $111.5-112.5^{\circ}$, and on oxidation with chromic acid in glacial acetic acid solution yields 4:4'-dichlorobenzophenone. 2:4':4''-Trichlorotriphenylmethane, $CH(C_6H_4Cl)_3$, prepared by reduction of the *carbinol* or its chloride with zinc dust and glacial acetic acid, melts at 106° . 2:4':4''-Trichlorotriphenylmethyl ethyl ether, $OEt \cdot C(C_6H_4Cl)_3$, prepared by treating the chloride with sodium ethoxide, crystallises slowly and melts at about 40° .

Tri-*p*-bromotriphenylchloromethane, $CCl(C_6H_4Br)_3$, is the main product of the action of carbon tetrachloride and aluminium chloride on bromobenzene; it crystallises in thin, hexagonal prisms, melts at 153° , and gives an orange-red coloration on addition of molecular silver to its solution in benzene. The *carbinol* crystallises in clear, transparent, hexagonal prisms and melts at 131° . The *ethyl ether*,



melts at 206° .

2:4':4''-Tribromotriphenylchloromethane, $C_{19}H_{12}ClBr_3$, formed in small amount from carbon tetrachloride and bromobenzene, or by diazotation of pararosanine, decomposition of the product with cuprous bromide, and treatment with hydrogen chloride in benzene solution, crystallises in small cubes, melts at $154-155^{\circ}$, and gives an intense purple colour with molecular silver in benzene solution; the *carbinol* melts at 134° ; the *ethyl ether*, $OEt \cdot C(C_6H_4Br)_3$, melts at $75-80^{\circ}$.

The action of molecular silver and air on the halogen-substituted triphenylchloromethanes in benzene solution leads to the formation of the corresponding peroxides, $\text{CR}_3 \cdot \text{O} \cdot \text{O} \cdot \text{CR}_3$ (compare Gomberg, *loc. cit.*). The position of the substituting halogen atoms only is given, the temperatures are melting points: *o-monochloro-*, 150° ; *m-monobromo-*, 170° ; *di-p-bromo-*, 174° ; *2:4':4''-trichloro-*, 140° ; *tri-p-chloro-*, 182° ; *tri-p-bromo-*, 192° ; *2:4':4''-tribromo-*, 153° .

These peroxides are obtained also in yields varying from 50—60 to 3—4 per cent. by the action of sodium peroxide on the carbinol chlorides.

Even after some years triphenylmethyl does not lose its power of absorbing oxygen and forming peroxides. In the action of molecular silver and air on the above substituted triphenylchloromethanes, the first product must be the unsaturated substance, the substituted triphenylmethyl, which in the second stage of the reaction absorbs oxygen.

A number of experiments are described to show that if the chloromethane is shaken for a short time with molecular silver and immediately exposed to air, the peroxide is formed, but if the shaking be too prolonged the molecular silver attacks the halogen atoms in the benzene nuclei. The velocity of the reaction varies with the number and nature of the halogens present. Connected with this are (1) the coloration formed when the molecular silver is added to the chloromethane in benzene solution, (2) the amount of halogen removed from the benzene nuclei, and (3) the nature of the resulting product. The results of determinations of (1) and (2) are given in tables. The *product* obtained on prolonged shaking of *2:4':4''-trichlorotriphenylchloromethane* with molecular silver and benzene is an amorphous, light yellow glass which is soluble in benzene or ether. Molecular weight determinations by the cryoscopic method give results which point to the removal of the chlorine being accompanied by the union of two of the triphenylmethyl molecules. This agrees better with Jacobson's than with Heintschel's formula for triphenylmethyl.

The authors conclude that the highly coloured, unstable derivatives of triphenylmethyl must be closely related to the stable triphenylmethane dyes. G. Y.

Removal of Chlorine from α -Chlorinated Fluorene Derivatives. HERMANN STAUDINGER (*Ber.*, 1906, 39, 3060—3062. Compare Gomberg, this vol., i, 414).—*Phenyldiphenylenemethyl* [*9-phenylfluoryl*] peroxide, $\text{C}_6\text{H}_4 \text{---} \text{C}_6\text{H}_4 \text{---} \text{CPh} \cdot \text{O} \cdot \text{O} \cdot \text{CPh} \text{---} \text{C}_6\text{H}_4 \text{---} \text{C}_6\text{H}_4$, separates after one to two days, when an ethereal solution of 9-chloro-9-phenylfluorene (obtained conveniently by saturating the carbinol in glacial acetic acid with hydrogen chloride; compare Kliegl, *Abstr.*, 1905, i, 187) is treated with amalgamated zinc in the presence of air and absence of moisture. It separates from benzene in crystals containing $2\text{C}_6\text{H}_6$, and melts at 194° .

9-Chlorofluorene under similar conditions yields *bisdiphenyleneethane*, which melts at 239° .

Ethyl diphenylenechloroacetate, obtained from phosphoric chloride

and ethyl diphenyleneglycolate, melts at 46—47°, does not react with zinc in ethereal solution, but with molecular silver yields *ethyl bis-diphenylenesuccinate*, $\begin{matrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{matrix} > \text{C}(\text{CO}_2\text{Et}) \cdot \text{C}(\text{CO}_2\text{Et}) < \begin{matrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{matrix}$, which separates from chloroform or benzene in large crystals and melts at 168—169°. C. S.

Dibenzyl-naphthalene. JOSEF J. VON BOGUSKI (*Ber.*, 1906, 39, 2866—2869).—When naphthalene and benzyl chloride are boiled for some time in the presence of a small quantity of aluminium powder, the products are α - and β -benzyl-naphthalene and a *dibenzyl-naphthalene*, $\text{C}_{24}\text{H}_{20}$. The last compound can be isolated from the fraction boiling at 250—273° under 33 mm. pressure. It forms slender, colourless, triclinic needles, melts at 146·5°, and dissolves in hot alcohol and in most organic solvents. J. J. S.

Preparation of a 3:4-Dichloroanilinesulphonic Acid. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 172461).—3:4-Dichloroaniline, when heated with a molecular proportion of sulphuric acid at 215°, yields a sulphonic acid which is probably 3:4-dichloroaniline-6-sulphonic acid. This substance is a white powder, soluble in 200 parts of hot and 1000 parts of cold water, which furnishes a sparingly soluble, colourless diazo-derivative and well-defined *sodium* salt, crystallising in large, lustrous leaflets. The *potassium* salt also crystallises readily; the *barium*, *zinc*, and *copper* salts are also soluble. G. T. M.

Reduction of Nitro-compounds by Alkaline Solutions of Stannous Oxide. HEINRICH GOLDSCHMIDT and MORITZ ECKARDT (*Zeit. physikal. Chem.*, 1906, 56, 385—452. Compare Goldschmidt and Ingebrechtsen, *Abstr.*, 1904, ii, 608; Goldschmidt and Sunde, this vol., i, 734).—The relation of the free to the combined alkali in alkaline solutions of stannous hydroxide has been ascertained by determining the solubility of the hydroxide in sodium hydroxide solutions of different strengths. From these determinations it appears that stannous hydroxide acts as a monobasic acid (compare Hantzsch, *Abstr.*, 1902, ii, 395), and that in sodium hydroxide solution it exists chiefly as the salt SnO_2HNa . A saturated solution of stannous hydroxide in pure water is found to contain 0·0000135 gram-mol. per litre, and when this result is combined with the values for the solubility in alkaline solutions, it appears that the affinity constant of stannous hydroxide as an acid is of the same order as that of phenol. The view that stannous hydroxide in sodium hydroxide solutions exists chiefly as the salt SnO_2HNa was confirmed by observing the catalytic effect of these solutions on the change of diacetonealcohol into acetone (see Koelichen, *Abstr.*, 1900, ii, 395). The stannous solutions were prepared by electrolysis of a solution of sodium hydroxide with a tin anode, and the course of the change of the diacetonealcohol into acetone was followed in a dilatometer. Similar experiments indicate that, when alkaline stannous hydroxide solutions are oxidised, the stannate produced contains sodium and tin in the atomic ratio 2:1.

The character of the reduction by alkaline stannous hydroxide solutions varies very much from one nitro-compound to another. Of the substances studied there are four which react with 3 molecules of stannous hydroxide, and yield amino-compounds directly: these are *o*- and *p*-nitrophenols and *o*- and *p*-nitroanilines. Other substances, namely, *m*-nitrophenol, *m*-nitroaniline, the three nitrobenzoic acids, the three nitrobenzenesulphonic acids, *p*-nitrotoluenesulphonic acid, and *o*-nitrobenzaldehyde, react with 2 molecules of stannous hydroxide. There is, however, further diversity, for whilst of the latter list *o*-nitrobenzoic acid and *o*-nitrobenzaldehyde lead to a hydroxylamine derivative as the end-product of the reaction, the others yield azo- and azoxy-compounds.

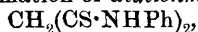
As regards the rate of reduction, the phenomena are simplest when the concentrations of tin and soda are low, and in these cases the velocity coefficient calculated for an equation of the second order is fairly constant. It is probable that the ion SnHO'_2 is the effective agent in the reduction, and that the nitro-compound is first reduced to a nitroso-compound, which in its turn is further reduced with infinitely great velocity. The value of the velocity coefficient rises markedly as the soda concentration is increased. This increase may be accounted for if it is assumed that in the more concentrated soda solutions disodium stannite is present.

In the following table are compared the values of the velocity coefficient of reduction for various nitro-compounds, (a) with alkaline stannous hydroxide solutions, (b) with stannous chloride and hydrochloric acid:

		Ortho.	Meta.	Para.
Nitroaniline	<i>a</i> ...	20	150	13·4
	<i>b</i> ...	0·655	0·175	0·10
Nitrophenol	<i>a</i> ...	5·72	40	1·57
	<i>b</i> ...	0·022	0·023	0·0022
Nitrobenzoic acid	<i>a</i> ...	97	130	226
	<i>b</i> ...	0·122	0·064	—
Nitrobenzenesulphonic acid	<i>a</i> ...	584	273	484
	<i>b</i> ...	0·052	0·073	0·129
Nitrobenzaldehyde	<i>a</i> ...	1030	—	—
	<i>b</i> ...	0·245	0·078	—

J. C. P.

Sulphur Derivatives of the Anilides of Malonic, Succinic, and Phenylacetic Acids and their Transformation Products. ARNOLD REISSERT and ARNOLD MORÉ (*Ber.*, 1906, **39**, 3298—3308. Compare Reissert, *Abstr.*, 1904, i, 990).—The action of phosphorus pentasulphide on malonanilide in boiling toluene solution in a reflux apparatus leads to the formation of *dithionmalonanilide*,



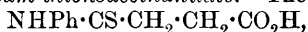
which crystallises from alcohol in yellow needles, melts at 149°, and is soluble in aqueous sodium hydroxide, but is insoluble in aqueous sodium carbonate. The *dithion-o-toluidide*, $\text{CH}_2(\text{CS}\cdot\text{NH}\cdot\text{C}_7\text{H}_7)_2$, prepared in the same manner from malon-*o*-toluidide, crystallises in yellow

needles and melts at 122—123°. The *dithion-p-toluidide*, $C_{17}H_{18}N_2S_2$, melts at 145°.

When shaken with cold concentrated sulphuric acid, dithionmalonanilide yields *dehydrodithionmalonanilide*, $CH_2 \begin{smallmatrix} \text{C(NPh)} \\ \text{C(NPh)} \end{smallmatrix} S_2$, which crystallises in matted, yellow needles, melts at 154—155°, and is insoluble in aqueous alkali hydroxides.

The action of hot dilute sulphuric acid on dithionmalonanilide leads to the formation of *dehydrodithionmalonanilide sulphide*, $S \left[CH \begin{smallmatrix} \text{C(NPh)} \\ \text{C(NPh)} \end{smallmatrix} S_2 \right]_2$, which crystallises in golden leaflets, melts and decomposes at 197°, and, when boiled with concentrated aqueous sodium hydroxide, yields a small amount of dithionmalonanilide, together with a substance, $C_{30}H_{22}N_4S_5$, melting at 210°.

Thionsuccinil, $\begin{smallmatrix} CH_2 \cdot CO \\ CH_2 \cdot CS \end{smallmatrix} > NPh$, is formed in only small amount by the action of phosphorus pentasulphide on succinil, but in good yields by boiling methyl succinilate with phosphorus pentasulphide in toluene solution. It separates from alcohol in stout, yellow crystals, melts at 116—117°, forms sodium sulphide when heated with aqueous sodium hydroxide, and when treated with cold alcoholic sodium hydroxide yields *sodium thionsuccinilate*. The free acid,



melts at 106—107°.

Methyl succinilate is prepared best by boiling succinil with concentrated sulphuric acid and methyl alcohol.

Benzothiazole-2-propionic acid, $C_6H_4 \begin{smallmatrix} S \\ N \end{smallmatrix} > C \cdot CH_2 \cdot CH_2 \cdot CO_2H$, formed by shaking thionsuccinilic acid with potassium ferricyanide in alkaline solution, crystallises in stout, white needles, melts at 108—109°, and is soluble in most organic solvents or dilute mineral acids. The *ammonium* and *silver* salts are described; the *methyl ester*, $C_{11}H_{11}O_2NS$, crystallises in soft, slender needles and melts at 57—58°; the *anilide*, $C_7H_4NS \cdot CH_2 \cdot CH_2 \cdot CO \cdot NPh$, forms colourless needles and melts at 149°; the *thionanilide*, $C_7H_4NS \cdot CH_2 \cdot CH_2 \cdot CS \cdot NPh$, formed by the action of phosphorus pentasulphide on the anilide in boiling xylene solution, crystallises in stout, yellow needles and melts at 127°.

s-Dibenzothiazylethane, $C_2H_4(C \begin{smallmatrix} S \\ N \end{smallmatrix} > C_6H_4)_2$ (Hofmann, Abstr., 1880, 388), is formed by oxidation of the preceding substance by means of potassium ferricyanide in alkaline solution.

Thionphenylacetoanilide, $C_{14}H_{13}NS$, prepared by the action of phosphorus pentasulphide on phenylacetanilide in boiling toluene solution, crystallises in long, soft, silky, yellow needles, melts at 88°, and is readily soluble in aqueous alkali hydroxides. G. Y.

Adipanilide. EYVIND BÖDTKER (*Ber.*, 1906, 39, 2765).—*Adipanilide*, $C_{18}H_{20}O_2N_2$, obtained by heating the acid and aniline at 190° for eight hours, crystallises from hot alcohol in glistening plates or feathery needles, melts at 240° (corr.), and dissolves in most organic solvents with the exception of ether. J. J. S.

ω -Sulphonic Acids and ω -Cyanides of Aromatic Amines.
 HANS BUCHERER and ARTHUR SCHWALBE (*Ber.*, 1906, 39, 2796—2813).
 —Sodium methylaniline- ω -sulphonate [*anilinomethanesulphonate*], $\text{NHPh}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}$, is obtained quantitatively by the interaction of formaldehyde bisulphite and aniline and converted into cyanomethylaniline by the action of potassium cyanide; the effect of steam, temperature, acids, and nitrous acid on the yields obtained in this reaction have been investigated. *Sodium monomethyl-p-toluidino- ω -sulphonate*, $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}$, crystallises in large platelets; the sodium salt of the *o*-toluidine derivative gives a flocculent precipitate, and the barium salt crystallises in plates. *Sodium monomethyl-o-anisidine- ω -sulphonate*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}$, crystallises in thick, voluminous platelets, the decomposition with potassium cyanide begins at 90° , and the ω -cyanomethyl-o-anisidine crystallises in glistening prisms melting at 68° . *Sodium monomethyl-p-nitroanilino- ω -sulphonate* separates in yellow needles and does not yield the nitrile.

The *disodium* salt of dimethyl-*m*-tolylene-2:4-diaminedi- ω -sulphonic acid crystallises in needles grouped in stellar aggregates; *di- ω -cyanodimethyltolylene-2:4-diamine* forms faintly yellow-coloured needles melting at 207° . *Sodium monomethyltolylene-2:4-diamine- ω -sulphonate* crystallises in diagonally-crossed needles, the nitrile separates as an oil. *Sodium dimethyl-p-phenylenediaminedi- ω -sulphonate* crystallises in rhombic plates, ω -cyanomonomethyl-p-phenylenediamine crystallises in plates melting at 168° ; the sodium salt of the corresponding sulphonate forms minute needles. *Sodium dimethylbenzidinedi- ω -sulphonate* separates in broad needles which are not altered by boiling with water; *di- ω -cyanodimethylbenzidine* melts at $241\text{--}242^\circ$; *sodium monomethylbenzidine- ω -sulphonate* separates in bundles of needles, whilst the corresponding ω -cyanomonomethylbenzidine crystallises in platelets melting at $142\text{--}144^\circ$ and forms a sparingly soluble diazo-compound which gives rise to red dyes.

ω -Cyanomethylanthranilic acid is a light yellow compound melting at 184° . *Sodium methyl- α -naphthylamine- ω -4-disulphonate* crystallises in prisms, *sodium- ω -cyanomethylnaphthionic acid* crystallises in well-formed plates which melt and become brown at 258° . *Sodium methyl- α -naphthylamine- ω -sulphonate* is a colourless, crystalline powder which becomes reddish-violet when exposed to damp air, ω -cyanomethyl- α -naphthylamine crystallises in long needles melting at 92° , whereas Knoevenagel (*Abstr.*, 1904, i, 989) found $44\text{--}45^\circ$. The corresponding ω -cyanomethyl- β -naphthylamine melts at $102\text{--}104^\circ$.

Sodium methylethylaniline- ω -sulphonate crystallises in thick plates and yields 75 per cent. of the nitrile, decomposing with potassium cyanide at 60° . Aniline and benzaldehydebisulphite condense to the sodium benzylaniline- ω -sulphonate described by Eibner (*Abstr.*, 1901, i, 376). ω -Cyanobenzyl-o-anisidine forms minute, glistening prisms melting at 73° .
 E. F. A.

Action of Bromine on Dimethylaniline. II. C. LORING JACKSON and LATHAM CLARKE (*Amer. Chem. J.*, 1906, 36, 409—414. Compare *Abstr.*, 1905, i, 768).—A repetition of the experiments

described in the earlier paper (*loc. cit.*) has shown that a mixture of dimethylaniline, bromine, and chloroform may give two entirely different products even when there is no apparent difference in the conditions of the reaction; thus sometimes the additive compound, $C_6H_5Br_2 \cdot NMe_2$, is produced, whilst at other times substitution occurs with formation of the compound $C_6H_4Br \cdot NMe_2$, HBr , Br , described by Fries (*Abstr.*, 1904, i, 571).

E. G.

A New Method of Preparing Aromatic Amines. FRANZ SACHS [and in part E. APPENZELLER, VIKTOR HEROLD, B. MYLO, KURT SCHÄDEL, and THEODOR SUTTER] (*Ber.*, 1906, **39**, 3006—3028).—In attempting to obtain evidence of the existence of the heteronuclear 2:6-naphthaquinone or its derivatives the author was led to a new method of preparing 5-amino- β -naphthol, which consisted in heating sodium β -naphthol-6-sulphonate with sodamide for forty minutes at 230 — 240° in a copper vessel fitted with a stirrer. In this way the sulphonic residue was eliminated and the NH_2 group introduced into a different position in the ring, and a yield of 51 per cent. of the product was obtained. The process was then extended to other derivatives of the aromatic hydrocarbons.

The sodium salts of benzenesulphonic and naphthalene- β -sulphonic acids when fused with sodamide furnished 30 and 32 per cent. of aniline and β -naphthylamine respectively. β -Naphthol-7-sulphonic acid gave rise to a mixture of isomeric aminonaphthols, in which 7-amino- β -naphthol and 5-amino- β -naphthol were identified. β -Naphthol-8-sulphuric acid also furnished a mixture of isomerides, which were partially separated by means of their benzoyl derivatives.

The basic salt of β -naphthol-1-sulphonic acid yielded a homogeneous product which, however, has not been identified with any of the known aminonaphthols.

α -Naphthol-5-sulphonic acid, when subjected to the sodamide fusion, furnished 5-amino- α -naphthol, which was characterised by the formation of a blue azo-dye with α -diazonaphthalene-4-sulphonic acid. 8-Amino- α -naphthol itself was not isolated from the sodamide fusion of α -naphthol-8-sulphonic acid, but was separated from the tarry by-products only in the form of its picrate.

Sodium anthraquinone- β -sulphonate, when fused with a mixture of sodamide and naphthalene, yielded anthranol, anthraquinone, and a base melting at 255° , which, although having the composition and molecular complexity of an aminoanthraquinone, is not identical with either α - or β -aminoanthraquinone.

β -Naphthol, when fused with sodamide and excess of naphthalene, yielded principally 6-amino- β -naphthol, together with small amounts of 7-amino- β -naphthol and the isomeride derived from β -naphthol-1-sulphonic acid; traces of naphthylenediamines were also discernible in the products of fusion.

α -Naphthol gave 5-amino- α -naphthol at 190° , at higher temperatures 1:5-naphthylenediamine results.

α -Naphthylamine, sodamide, and naphthalene, when fused for thirty minutes at 230° , give a 47 per cent. yield of pure 1:5-naphthylenediamine; hydrogenated naphthalenes are produced when the heating is prolonged.

β -Naphthylamine under similar conditions gives 2:5-naphthylene-diamine and a trace of an ortho-diamine, probably 2:3-naphthylene-diamine.

When naphthalene, phenol, and sodamide are fused at 200—220°, amino-groups are introduced into the naphthalene nucleus, and α -naphthylamine and 1:5-naphthylenediamine are produced, and similar results are obtained when resorcinol or sulphanilic acid are employed in the fusion instead of phenol.

The following substances were employed in characterising the amino-naphthols: dibenzoyl-1-amino- β -naphthol, silky needles, melting point 235.5° (compare *Trans.*, 1889, 55, 121); N-benzoyl-3-amino- β -naphthol, hexagonal plates, melting point 233.5°; dibenzoyl-4-amino- β -naphthol, rhombic plates, melting at 309—310°; dibenzoyl-5-amino- β -naphthol, white needles, melting at 223°; N-benzoyl-5-amino- β -naphthol, white needles, melting at 152°; diacetyl-5-amino- β -naphthol, melting at 187°; acetyl-5-amino-2-methoxynaphthalene, felted needles, melting at 140°; 5-amino- β -naphthol picrate, yellow needles, melting point 183°; dibenzoyl-6-amino- β -naphthol, prisms, melting at 233.5°; dibenzoyl-7-amino- β -naphthol, white needles, melting at 187.5°; dibenzoyl-8-amino- β -naphthol, white prisms, melting at 208°; dibenzoyl-4-amino- α -naphthol, rhombic crystals, melting at 215°; dibenzoyl-5-amino- α -naphthol, rhombic plates, melting at 276°.

The following derivatives of 1:8-naphthylenediamine were prepared: dibenzoyl-1:8-naphthylenediamine, needles, melting at 311—312°; ethylidene-1:8-naphthylenediamine, crystallising from dilute alcohol in green needles and decomposing at 210°.

2:6-Dihydroxynaphthalene, when treated with oxidising agents such as ferric chloride, potassium dichromate, ammonium persulphate, manganese dioxide and sulphuric acid, potassium permanganate and potassium hypobromite, furnishes yellowish-white precipitates which dissolve in aqueous alkalis to a green solution; the analytical data and molecular determinations of their oxidation products agree approximately with the formula $(C_{10}H_5O_2)_4$.
G. T. M.

Substituted Diphenylhydroxylamines. HEINRICH WIELAND and STEPHAN GAMBARJAN (*Ber.*, 1906, 39, 3036—3042. Compare this vol., i, 453). — *p*-Nitrosodiphenylhydroxylamine, $NO \cdot C_6H_4 \cdot N(OH) \cdot C_6H_5$, prepared by Bamberger's method from nitrosobenzene and cold concentrated sulphuric acid, was converted into its *methyl ether* by shaking with methyl sulphate and dilute aqueous sodium hydroxide; this melted at 137—138° without decomposition; it is soluble in all the organic media. It is markedly basic, and when warmed with moderately concentrated sulphuric acid it undergoes hydrolysis and nitrosobenzene is produced. On reduction either with zinc dust and acetic acid or alcoholic hydrogen sulphide, it yields *p*-aminodiphenylamine.

These reactions are most readily explained on the supposition that *p*-nitrosodiphenylhydroxylamine is a pseudo-acid, which, on the formation of a salt, assumes the quinonoid *aci*-form, $HO \cdot N : C_6H_4 \cdot \overset{N \cdot C_6H_5}{\underset{O}{\text{<}}}$, and yields a methyl ether having a similar constitution.

2 : 4-Dinitrodiphenylhydroxylamine, $C_6H_5 \cdot N(OH) \cdot C_6H_3(NO_2)_2$, is formed together with dinitrodiphenylamine and aniline when 1-bromo-2 : 4-dinitrobenzene and phenylhydroxylamine are heated in alcoholic solution in a reflux apparatus. It separates from benzene in flattened, orange-coloured needles melting and decomposing at $114-115^\circ$, is readily soluble in most organic media excepting petroleum, and is scarcely soluble in water. In aqueous solutions of ammonia or the alkali hydroxides, it furnishes soluble, brownish-red salts corresponding with the quinonoid *aci*-form. On reduction with zinc dust and acetic acid, diaminodiphenylamine is produced. G. T. M.

Benzoyl-*p*-bromophenylcarbamide : a By-product in the Preparation of Benzoylbromoamide. FORRIS J. MOORE and A. M. CEDERHOLM (*J. Amer. Chem. Soc.*, 1906, 28, 1190—1198).—When benzoylbromoamide is prepared by Hoogewerff and van Dorp's method (Abstr., 1889, 981), it is liable to contain as much as 10 per cent. of benzoyl-*p*-bromophenylcarbamide.

*Benzoyl-*p*-bromophenylcarbamide*, $C_6H_4Br \cdot NH \cdot CO \cdot NHBz$, crystallises in silky needles, melts at 230° in a closed tube, decomposes at 232° , and is soluble in glacial acetic acid and insoluble in water or ether. The compound can be synthesised (1) by the action of phenylcarbamide on benzoylbromoamide in benzene solution, (2) by the action of *p*-bromophenylcarbimide on benzoylbromoamide in alkaline solution, (3) by heating a mixture of *p*-bromophenylcarbimide and benzamide, and (4) by the action of benzoylbromoamide on benzoylphenylcarbamide in benzene solution.

The production of benzoyl-*p*-bromophenylcarbamide in the preparation of benzoylbromoamide is regarded as due to the formation of benzoylphenylcarbamide in the course of the reaction and its subsequent bromination by the benzoylbromoamide itself. E. G.

Action of Bases on Thiocarbamides. REINHOLD VON WALTHER and A. STENZ (*J. pr. Chem.*, 1906, [ii], 74, 222—231. Compare Abstr., 1900, i, 569).—The action of ammonium acetate on *s*-diphenylthiocarbamide in glacial acetic acid solution on the water-bath leads to the formation of hydrogen sulphide and *s*-diphenylcarbamide, but in alcoholic solution to the formation of phenylthiocarbamide.

When heated with hydroxylamine hydrochloride in acetic acid solution, *s*-diphenylthiocarbamide yields *s*-diphenylcarbamide, aniline, and carboxyl sulphide; phenyloxythiocarbamide, formed as an intermediate product in this reaction, yields *s*-diphenylcarbamide, aniline, and carbonyl sulphide when heated with glacial acetic acid.

When heated with hydroxylamine in alcoholic solution, *s*-diphenylthiocarbamide forms sulphur and aniline.

s-Diphenylcarbamide, acetanilide, and hydrogen sulphide are formed by heating guanidine with *s*-diphenylthiocarbamide in glacial acetic acid solution (compare Bamberger, Abstr., 1881, 43).

The action of hydrazine on *s*-diphenylthiocarbamide in alcoholic solution on the water-bath leads to the formation of hydrazodicarbonthiophenylamide, together with small amounts of hydrogen sulphide and a substance, $C_{14}H_{12}N_4S$, which is obtained also by boiling

2 mols. of *s*-diphenylthiocarbamide with 1 mol. of hydrazine in glacial acetic acid solution; it crystallises in yellow leaflets and melts at 237°.

When boiled with *o*-toluidine in alcoholic solution for one hour, or in glacial acetic acid solution for ten minutes, *s*-diphenylthiocarbamide forms aniline and *ab*-phenyl-*o*-tolylthiocarbamide; *ab*-phenyl-*m*-tolylthiocarbamide is formed in the same manner from *s*-diphenylthiocarbamide and *m*-toluidine.

ab Phenyl-*p*-tolylthiocarbamide melts at 141°; the substance melting at 158° (*loc. cit.*) is a mixture of homologous thiocarbamides (compare Kjellin, Abstr., 1903, i, 287; Hegershoff, *ibid.*, 477). This mixture is formed also by the action of *p*-toluidine on phenylthiocarbimide.

When heated with phenylhydrazine in alcoholic or acetic acid solution, or without a solvent, *s*-diphenylthiocarbamide forms diphenylthiosemicarbazide melting at 177° (Walther, Abstr., 1896, i, 534).

1-Phenyl-4-*p*-tolylthiosemicarbazide formed by heating di-*p*-tolylthiocarbamide, or *ab*-phenyl-*p*-tolylthiocarbamide with phenylhydrazine in glacial acetic acid solution, melts at 165° and remains unchanged when heated with alcoholic hydrogen chloride (compare Marckwald, Abstr., 1893, i, 26; 1899, i, 503).

1-Phenyl-4-*o*-tolylthiosemicarbazide formed from *ab*-phenyl-*o*-tolylthiocarbamide, melts at 156°.

Diphenylmethylthiosemicarbazide is obtained by heating *s*-diphenylthiocarbamide with phenylmethylhydrazine in glacial acetic acid solution; 1:4-diphenylthiosemicarbazide is formed by heating guanyphenylthiocarbamide with an excess of phenylhydrazine. G. Y.

Behaviour of Carboxylic Acids towards Phenylcarbimide.

WALTER DIECKMANN and FRITZ BREET (*Ber.*, 1906, 39, 3052—3055). —The action of phenylcarbimide on carboxylic acids leads to the formation of mixed anhydrides, $\text{RCO}\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$, of phenylcarbamic acid and the corresponding carboxylic acid.

Lævulic acid and phenylcarbimide when mixed in molecular proportions yield a colourless, crystalline mass of the mixed *anhydride*, $\text{CMeO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$. This substance, when freshly prepared, is readily soluble in dry ether; it is, however, somewhat unstable and is decomposed into lævulic acid and diphenylcarbamide by water, and by cold alcohol into lævulic acid and ethyl phenylcarbamate. Ammonia resolves it into lævulic acid and diphenylcarbamide. The anhydride evolves carbon dioxide slowly at the ordinary temperature, rapidly at 100°, diphenylcarbamide and lævulic anhydride being produced; some angelicalactone was also noticed. Ethyl lævulate does not interact with phenylcarbimide.

β -Benzoylpropionic acid forms a similar mixed anhydride with phenylcarbimide. The additive compound from phenylacetic acid and phenylcarbimide is a colourless, crystalline mass, which is decomposed by water, alcohol, or ammonia. The spontaneous decomposition of this product at the ordinary temperature is complete within forty-eight hours, carbon dioxide is evolved, and the residue consists chiefly of phenylacetanilide together with some diphenylcarbamide and phenylacetic anhydride.

Acetic acid and phenylcarbimide combine with generation of heat to form an additive compound, which is decomposed in about twenty-four hours at the ordinary temperature into carbon dioxide and acetanilide, together with a certain amount of diphenylcarbamide and acetic anhydride.

Dihydrocinnamic acid and phenylcarbimide furnish a crystalline additive compound which slowly evolves carbon dioxide at the ordinary temperature. At 100° it decomposes into carbon dioxide, diphenylcarbamide, and dihydrocinnamic anhydride, whilst at 180° dihydrocinnamanilide is the chief product. Water, alcohol, and ammonia decompose the mixed anhydride regenerating dihydrocinnamic acid.

The additive products from cinnamic and benzoic acids have similar properties. G. T. M.

Ozonides of Hydro-aromatic Compounds and the Stability of Different Ring Systems. CARL D. HARRIES and HEINRICH NERESHEIMER (*Ber.*, 1906, **39**, 2846—2850. Compare *Abstr.*, 1904, i, 361, this vol., 261).—*Tetrahydrobenzeneozonide*, $C_6H_{10}O_3$, obtained by passing ozone into a chloroform solution of the unsaturated hydrocarbon, forms elastic lumps sparingly soluble in all ordinary solvents. When boiled for some time with water it yields a considerable amount of *n*-adipic acid and a small amount of the corresponding aldehyde.

m-Dihydro-xylene (Verley, *Abstr.*, 1898, i, 557) yields a *diozonide* $C_6H_6Me_2O_3$, which, after repeated solution in ethyl acetate and precipitation with light petroleum, forms a water-clear syrup with a characteristic odour. It dissolves readily in most organic solvents, is comparatively stable, but occasionally explodes with great violence. When reduced it yields lævulinaldehyde, and hence the hydrocarbon is probably 1:3-dimethyl- $\Delta^{2:6}$ -cyclohexadiene.

The ozonides of hydroaromatic compounds are much more stable than those derived from benzene compounds. Ring systems containing more than six carbon atoms yield ozonides, which are far less stable than those derived from hydroaromatic compounds. J. J. S.

Pseudo-acids. ARTHUR HANTZSCH (*Ber.*, 1906, **39**, 2703—2705).—A reply to Euler (compare this vol., i, 576). C. S.

Constitution and Colour of Nitrophenols. ARTHUR HANTZSCH (*Ber.*, 1906, **39**, 3072—3080. Compare this vol., i, 353).—Polemical. A reply to Kauffmann (this vol., i, 577). C. S.

Action of *tert.*-Alkyl Chlorides on *p*-Nitrophenol Salts. LEOPOLD SPIEGEL and H. KAUFMANN (*Ber.*, 1906, **39**, 2638—2640).—In studying the etherification of *p*-nitrophenol with various alcohols, Spiegel and Sabbath (*Abstr.*, 1901, i, 533) attempted without success to prepare the *tert.*-butyl ether, decomposition taking place at higher temperatures, whilst at lower temperatures the silver salt of *p*-nitrophenol was converted into *p*-nitrophenol by the action of

tert.-butyl chloride. The fact, however, that the silver salt in question contains water of crystallisation was overlooked at the time, so that action took place according to the equation $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OAg} + \text{H}_2\text{O} + \text{CMe}_3\text{Cl} = \text{AgCl} + \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH} + \text{CMe}_3 \cdot \text{OH}$.

The silver salt is unsuitable for the formation of the tertiary ether, since it does not become anhydrous when heated at 100° , and it decomposes explosively at 110° . The sodium salt, on the other hand, may be dehydrated completely at 120 — 130° , changing its tint from bright yellow to dark red in the process. When sodium *p*-nitrophenol, *tert.*-butyl chloride, and *tert.*-butyl alcohol are heated at 110° for six hours, sodium chloride and *p*-nitrophenol are obtained. At the same time isobutylene is formed by elimination of hydrogen chloride from the butyl chloride; it was identified by the formation of $\alpha\beta$ -dibromo- β -methylpropane, $\text{CMe}_2\text{Br} \cdot \text{CH}_2\text{Br}$, by the action of bromine.

A. McK.

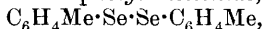
Solution Equilibrium between 2:4-Dinitrophenol and Aniline. ROBERT KREMAN (Monatsh., 1906, 27, 627—630. Compare Abstr., 1905, ii, 77; Noelting and Sommerhoff, this vol., i, 157).—The melting-point curve for mixtures of 2:4-dinitrophenol and aniline drops from the melting point of the former and has a break representing a compound melting at 75° .

The influence of the two nitro-groups in the meta-position to each other is greater than that of the nitro- and hydroxy-groups in the ortho-position, as *o*-nitrophenols as such do not form compounds with aniline.

G. Y.

Selenium Compounds. F. TABOURY (Bull. Soc. chim., 1906, [iii], 35, 668—674. Compare Abstr., 1903, i, 748).—Selenium reacts readily with magnesium alkyl haloids, and the complexes formed yield on treatment (1) with dilute acids, selenophenols and diselenides; (2) with acid chlorides or anhydrides, esters of the series of acids typified by $\text{R} \cdot \text{CO} \cdot \text{SeH}$; and (3) with alkyl iodides, mixed selenides. The compounds formed are strictly analogous with those obtained by the action of sulphur on magnesium alkyl haloids (Abstr., 1903, i, 748; 1904, i, 493; 1905, i, 56, 644).

Selenophenol boils at 182° (compare Krafft and Lyons, Abstr., 1894, i, 448). Phenyl diselenide melts at 62° (*loc. cit.*). α -Selenonaphthol, $\text{C}_{10}\text{H}_7 \cdot \text{SeH}$, is a slightly yellow liquid, boils at 165 — 167° under 20 mm. pressure, and evolves hydrogen selenide when heated at atmospheric pressure. α -Naphthyl diselenide, $\text{C}_{10}\text{H}_7 \cdot \text{Se} \cdot \text{Se} \cdot \text{C}_{10}\text{H}_7$, separates from alcohol in orange-yellow prisms and melts at 87 — 88° . Benzyl α -naphthyl selenide forms small, colourless prisms, melts at 68 — 69° , and yields a *picrate* which separates from ether in orange-red needles and melts at 118° . *p*-Selenocresol, $\text{C}_6\text{H}_4\text{Me} \cdot \text{SeH}$, crystallises from ether in colourless lamellæ, melts at 46 — 47° , and rapidly oxidises on exposure to air to *p*-tolyl diselenide,



which separates from alcohol in orange needles and melts at 47° . Benzyl-*p*-tolyl selenide, $\text{CH}_2\text{Ph} \cdot \text{Se} \cdot \text{C}_6\text{H}_4\text{Me}$, forms small, unctuous, colourless lamellæ and melts at 32 — 33° . *p*-Tolyl selenobenzoate,

$\text{COPh}\cdot\text{Se}\cdot\text{C}_6\text{H}_4\text{Me}$, crystallises in colourless prisms, melts at $71-72^\circ$, and reddens on exposure to light, due to the liberation of selenium. *p*-Bromoselenophenol separates from ether in colourless lamellæ, melts at about $75-77^\circ$ and oxidises rapidly on exposure to air, forming *p*-dibromobenzene diselenide, $\text{C}_6\text{H}_4\text{Br}\cdot\text{Se}\cdot\text{Se}\cdot\text{C}_6\text{H}_4\text{Br}$, which forms yellow needles from alcohol and melts at $107-108^\circ$. *p*-Chloroselenophenol forms small, colourless lamellæ, melts at about 55° , and rapidly oxidises in air to *p*-dichlorobenzene diselenide, yellow needles, melting at $85-86^\circ$. *p*-Methoxyphenyl selenobenzoate, $\text{COPh}\cdot\text{Se}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, forms colourless crystals from alcohol and melts at 97° . *p*-Ethoxyselenophenol is a colourless liquid, heavier than water, boils at $156-158^\circ$ under 24 mm. pressure, and on oxidation of its solution in dilute potassium hydroxide yields *p*-diethoxyphenyl diselenide, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{Se}\cdot\text{Se}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, which crystallises in brilliant yellow lamellæ and melts at 65° . *p*-Ethoxyphenyl selenobenzoate separates from light petroleum in needles and melts at $94-95^\circ$.
T. A. H.

Nitrophenolsulphonic Acids. ROBERT GNEHM and OSKAR KNECHT (*J. pr. Chem.*, 1906, [ii], 74, 92—111. Compare this vol., i, 578; Franklin, Abstr., 1898, i, 522).—The action of sulphuryl chloride on *o*-nitroanisole leads to the formation of *p*-chloro-*o*-anisole, that of sulphuryl chloride and aluminium chloride to the formation of 4-chloro-2-nitrophenol and 4:6-dichloro-2-nitrophenol, and that of chlorosulphonic acid to the formation of *o*-nitroanisole-*p*-sulphonic acid together with a small amount of *p*-chloro-*o*-nitroanisole.

o-Nitroanisole-*p*-sulphonic acid crystallises from water in glistening, transparent plates, or from a mixture of ethyl acetate and benzene in white needles or large, glistening prisms. The ammonium and barium (+7H₂O) salts are described. *o*-Nitroanisole-*p*-sulphonyl chloride, $\text{C}_7\text{H}_6\text{O}_5\text{NClS}$, is prepared by the action of phosphorus pentachloride on ammonium *o*-nitroanisole-*p*-sulphonate on the water-bath, or by the action of nitric acid of sp. gr. 1.475 on anisole-*p*-sulphonyl chloride at -7° to -5° ; it crystallises from a mixture of benzene and light petroleum in slender, white needles, melts at 66° , and is hydrolysed on prolonged boiling with water. *o*-Nitroanisole-*p*-sulphonamide, $\text{C}_7\text{H}_8\text{O}_5\text{N}_2\text{S}$, prepared by the action of ammonium carbonate on the sulphonyl chloride, crystallises in long, yellowish-white needles and melts at 146.3° .

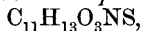
Methyl o-nitroanisole-*p*-sulphonate, $\text{C}_8\text{H}_9\text{O}_6\text{NS}$, is obtained in only small amount by the action of an excess of methyl alcohol, whilst sodium *o*-nitroanisole-*p*-sulphonate is formed by the action of sodium methoxide in methyl-alcoholic solution on the sulphonyl chloride. The methyl ester is prepared in good yields by the action of sodium methoxide free from methyl alcohol, on the sulphonyl chloride in benzene solution; it crystallises in glistening, colourless prisms, melts at 83° , and is partially hydrolysed on recrystallisation from water, the unchanged ester separating in thin, white needles.

o-Anisidine-*p*-sulphonic acid, $\text{C}_7\text{H}_9\text{O}_4\text{NS}$, prepared by the reduction of *o*-nitroanisole-*p*-sulphonic acid by means of tin and hydrochloric acid, crystallises in glistening, thin needles, dissolves in water, becoming brown on oxidation by the air, gives a Bordeaux-red color-

tion with ferric chloride, reduces silver nitrate solutions, and forms readily soluble salts; nitrous acid or amyl nitrite converts it into the *diazo*-derivative, which couples with β -naphthol in alkaline solution, forming a bluish-red *azo-dye*. Complete reduction of *o*-nitroanisole-*p*-sulphonyl chloride by means of hydriodic acid, zinc dust and sulphuric acid, or tin and hydrochloric acid leads to the formation of *m*-amino-*p*-methoxythiophenol, which is isolated as the *hydrochloride*, $C_7H_9ONS \cdot HCl$; this crystallises in white, odourless needles, becomes brown at 170° , melts, forming a red liquid, at 230 — 235° , and is readily soluble in water or aqueous sodium hydroxide. The *mercuric* and *lead* salts are described. The free thiophenol forms stout, yellow, glistening crystals, is unstable, and is rapidly oxidised to the *disulphide hydrochloride*, $S_2[C_6H_3(OMe) \cdot NH_2]_2$, which forms white crystals and dissolves slowly in water. The *disulphide* separates from a mixture of toluene and light petroleum in spherical crystals, becomes violet on exposure to air, and gives with concentrated sulphuric acid a light green coloration changing through dark green to dark blue on warming. The action of nitrous acid on *m*-amino-*p*-methoxythiophenol leads to the formation of the *diazo*-derivative of the disulphide; this couples with β -naphthol in alkaline solution, forming a blood-red *azo-dye*, $S_2[C_6H_3(OMe) \cdot N_2 \cdot C_{10}H_6 \cdot OH]_2$.

In presence of sodium acetate, the thiophenol hydrochloride condenses with picryl chloride in boiling alcoholic solution, forming the *product*, $S_2[C_6H_3(OMe) \cdot NH \cdot C_6H_2(NO_2)_3]_2$, which crystallises in bluish-red, microscopic needles, and when heated melts, forming a red liquid, detonating at higher temperatures.

The *diacetyl* derivative of *m*-amino-*p*-methoxythiophenol,



prepared by heating the hydrochloride with sodium acetate, zinc dust, and acetic anhydride, crystallises in glistening, transparent plates and melts at 85 — 86° .

Nitration of anisole-*p*-sulphonamide (compare Franklin, *loc. cit.*) leads to the formation of *m*-dinitrobenzene and a syrup which, on treatment with ammonia, yields *o*-nitroanisole-*p*-sulphonamide identical with the product obtained from *o*-nitroanisole.

The oxidation of a mixture of *m*-amino-*p*-methoxythiophenol hydrochloride and dimethyl-*p*-phenylenediaminethiosulphonic acid by means of potassium dichromate in dilute acetic acid solution at 0° leads to the formation of an *indaminethiosulphonic acid*, which forms a reddish-violet solution becoming blue and finally green as the oxidising agent is added, and when boiled with zinc chloride solution is converted into

the *thiazine dye*, $S_2 \left[C \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} \text{CH} \cdot C(NH_2) : C(OMe) \end{array} \begin{array}{c} \text{C} : N : C : CH : CH \\ \text{C} : S : C : CH : C : NMe_2 \end{array} \right]_2$.

This is obtained as a dark violet-blue powder with copper lustre, is slightly soluble in hot water, forming a violet-blue solution, gives red to blue flocculent precipitates with dilute hydrochloric or nitric acid, sodium carbonate or hydroxide, or ammonia, is decolorised by stannous chloride in hydrochloric acid solution, and with aqueous sodium sulphide forms a red, flocculent precipitate which is decolorised on heating. It dyes unmordanted cotton wool only feebly, more strongly in presence of sodium sulphide; cotton wool mordanted with tannin

is dyed a pure blue, fast to washing. A table is given showing the results of the spectroscopic examination of the dye. The *acetyl* derivative of the leuco-compound is obtained as an impure yellowish-brown powder melting at 120—121°.

A *résumé* is given of the views of previous authors as to the constitution of the sulphur dyes. G. Y.

Aminophenolsulphonic and Aminocresolsulphonic Acids. GUSTAV SCHULTZ (*Ber.*, 1906, 39, 3345—3347).—Aminophenol-sulphonic acid III, formed by heating the anilinedisulphonic acid prepared from *m*-aminobenzenesulphonic acid with sodium hydroxide under pressure, is 3-aminophenol-4-sulphonic and not 3-aminophenol-6-sulphonic acid, whilst the anilinedisulphonic acid has the sulphonic groups in the positions 3:6 and not 3:4, as it readily yields benzene-*p*-disulphonic acid when converted into the corresponding hydrazine and boiled with aqueous cupric sulphate.

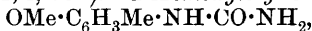
The *anilide*, $C_6H_4(SO_2 \cdot NHPh)_2$, crystallises in nacreous leaflets and melts at 249°.

When diazotised and boiled with alcohol, 3-aminophenol-4-sulphonic acid yields an *ethoxyphenolsulphonic acid*. G. Y.

Preparation of a Di-*o*-anisidinedisulphonic Acid. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 172106).—Benzidine and tolidine on sulphonation furnish complex mixtures of mono- and di-sulphonic acids, sulphones, and sulphonesulphonic acids. It has now been discovered that di-*o*-anisidine, on the contrary, readily yields a homogeneous product consisting of a disulphonic acid when the reaction is effected at low temperatures.

The base is dissolved in four parts of fuming sulphuric acid (10 per cent. of SO_3) below 4°; subsequently the solution is heated slowly to 20—25° and then poured on to ice. The *di-*o*-anisidine-6:6'-disulphonic acid*, $C_{12}H_4(OMe)_2(NH_2)_2(SO_3H)_2$ [3:3':4:4':6:6'], which is somewhat soluble in water, is isolated in the form of its sparingly soluble normal *sodium* salt, this compound separating from its aqueous solution in silvery leaflets containing water of crystallisation. The acid itself is a white, crystalline substance, which may be employed in the production of colouring matters. G. T. M.

Ethers of Aminocresols and their Derivatives. LEOPOLD SPIEGEL, N. MUNBLIT, and H. KAUFMANN (*Ber.*, 1906, 39, 3240—3251. Compare *Abstr.*, 1901, i, 533).—2-Methoxytolyl-3-carbamide,



obtained from 3-amino-2-methoxytoluene hydrochloride and carbamide on the water-bath, melts at 150°, and does not have a sweet taste. The corresponding *thiocarbamide*, $C_9H_{12}ON_2S$, melts at 137°.

3-Amino-2-ethoxytoluene is a yellow oil; the *hydrochloride*, $C_9H_{13}ON \cdot HCl$, melts at 189°, the *carbamide* at 183°, the *thiocarbamide* at 140°.

3-Nitro-2-propoxytoluene, obtained from the potassium salt of the nitrocresol and propyl bromide in propyl alcohol at 160°, is a yellow

oil, which boils at 210—212°. The *amino*-compound is a colourless liquid, the *hydrochloride* of which melts at 178°. The *carbamide*, $C_{11}H_{16}O_2N_2$, forms colourless needles and does not have a sweet taste; the *thiocarbamide* melts at 124°.

The *allyl ether* of 3-nitro-2-cresol is a yellow oil; the *amino*-compound is a red oil; the *hydrochloride* melts at 160°. The *carbamide*, obtained from the preceding salt and potassium cyanate, melts at 137°; the *thiocarbamide* at 130°.

The *benzyl ether* of 3-nitro-2-cresol is a red oil. The *amino*-compound, obtained by reduction with iron and 1 per cent. acetic acid solution, forms a *hydrochloride*, which melts at 178°. The *carbamide* melts at 113° and does not have a sweet taste.

2-Ethoxytolyl-5-carbamide melts at 158°.

4-Nitro-2-ethoxytoluene melts at 61°, the *amino*-compound boils at 249—250°, and the *hydrochloride* melts at 245°. The *carbamide* melts at 161°; the *thiocarbamide* melts at 198° and has a bitter taste.

2-Ethoxytolyl-4-hydrazine, $OEt \cdot C_7H_6 \cdot NH \cdot NH_2$, obtained by the reduction of the diazotised ethoxytoluidine hydrochloride, is an oil with the odour of phenylhydrazine. The *hydrochloride* melts and decomposes at 185—186°, and in aqueous solution yields, with dextrose and sodium acetate, 2-ethoxytolyl-4-d-glucosazone, $C_{24}H_{34}O_6N_4$, which forms microscopic, yellow crystals and melts at 168°.

Ethyl 2-ethoxytolyl-4-carbamate, $OEt \cdot C_7H_6 \cdot NH \cdot CO_2Et$, obtained from an ethereal solution of ethyl chlorocarbonate and the ethoxytoluidine, melts at 68°.

The *ethylene ether* of 4-nitro-2-cresol, $C_2H_4(O \cdot C_7H_6 \cdot NO_2)_2$, obtained from the potassium salt and ethylene dibromide, forms yellow needles and melts at 202°. The *amino*-compound, $C_{16}H_{20}O_2N_2$, melts at 129°; the *carbamide*, $C_{13}H_{22}O_4N_4$, melts at 218° and has a faint, bitter taste.

C. S.

Constitution of Pseudo-phenols. KARL AUWERS (*Ber.*, 1906, 39, 3160—3181).—The author had suggested previously a phenolic structure for pseudo-phenols, whereas Zincke sometimes accepts the phenolic structure and sometimes the desmotropic ketonic structure. In the present paper, the author considers the question from the cryoscopic standpoint.

Pseudo-phenols of the type $CH_2X \cdot C \begin{smallmatrix} \swarrow C(OH):CH \\ \searrow CH-CX \end{smallmatrix} > CH$, where X and X' were negative substituents, were studied.

When 5-nitro-2-hydroxybenzyl chloride, melting at 128°, was boiled in acetic acid solution with sodium acetate, 5-nitro-2-hydroxybenzyl acetate, $OAc \cdot CH_2 \cdot C_6H_3(NO_2) \cdot OH$, is formed; it separates from benzene in brown crystals and melts at 106.5—108.5°.

5-Nitro-2-hydroxybenzyl bromide, $CH_2Br \cdot C_6H_3(NO_2) \cdot OH$, prepared by passing a current of hydrogen bromide into a solution of either of the two preceding compounds at 70—80°, separates from benzene in leaflets and melts at 147°. By the action of bromine it forms 3-bromo-5-nitrobenzyl bromide, $NO_2 \cdot C_6H_3Br \cdot CH_2Br$, which separates from glacial acetic acid in needles and melts at 155°. The 6-bromo-derivative of 5-nitro-o-cresol, $C_7H_6O_3NBr$, prepared in a similar manner,

separates from glacial acetic acid in needles and melts at 118·5—119·5°.

Ethyl ω-chloro-6-hydroxy-m-toluate, $\text{CH}_2\text{Cl}\cdot\text{C}_6\text{H}_3(\text{CH}_2\text{Cl})\cdot\text{CO}_2\text{Et}$, separates from benzene in needles and melts at 119·5°. Its *bromo-*derivative separates from glacial acetic acid in needles and melts at 142—143°.

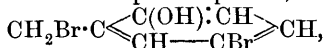
Ethyl 6-hydroxy-m-toluate, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}_2\text{Et}$, prepared by oxidising the corresponding hydroxy-aldehyde by fusion with potash and then esterifying the acid formed, separates from a mixture of benzene and light petroleum in pink needles and melts at 98—99°.

3-Nitro-4-hydroxybenzyl chloride, $\text{CH}_2\text{Cl}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{OH}$, melts at 75°, whereas the corresponding bromide, $\text{C}_7\text{H}_6\text{O}_3\text{NBr}$, obtained by passing a current of hydrogen bromide into a warm solution of the corresponding alcohol in acetic acid, melts at 83—85° and separates from glacial acetic acid in yellow needles.

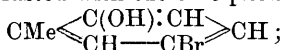
Details of the cryoscopic determinations, which were conducted partly in benzene and partly in *p*-dibromobenzene solutions, are appended.

m-Bromo-*o*-hydroxybenzyl bromide behaves towards phenylcarbimide as a hydroxylic substance to form the *urethane*, $\text{C}_{14}\text{H}_{11}\text{O}_2\text{NBr}_2$, which crystallises in silky needles and melts at 170—171°.

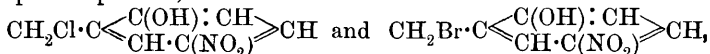
A comparison of the pseudo-phenols and their parent true phenols with regard to cryoscopic behaviour indicates that the pseudo-phenols are phenolic in structure. The pseudo-phenol,



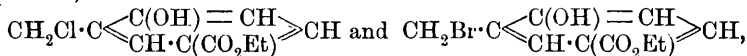
was, for example, contrasted with the true phenol,



the pseudo-phenols,



with the true phenol, $\text{CMe}\cdot\text{C}\begin{array}{c} \diagup \text{C(OH):CH} \\ \text{CH}\cdot\text{C(NO}_2) \end{array} \text{CH}$; and the pseudo-phenols,



with the true phenol, $\text{CMe}\cdot\text{C}\begin{array}{c} \diagup \text{C(OH)=CH} \\ \text{CH}\cdot\text{C(CO}_2\text{Et)} \end{array} \text{CH}$.

The author discusses at length the constitution of pseudo-phenols, and criticises in particular the views of Zincke. A. McK.

8-Amino-1-naphthol. FRITZ FICHTER and RUDOLF GAGEUR (*Ber.*, 1906, 39, 3331—3339. Compare Friedländer and Silberstern, *Abstr.*, 1902, i, 793).—8-Acetylamino-1-naphthol, prepared by treating 8-amino-1-naphthol with finely-powdered sodium acetate, acetic anhydride, and glacial acetic acid, crystallises in colourless, broad needles or plates, melts at 168—169° (138°: Friedländer and Silberstern, *loc. cit.*), and boils at 170—172° under 16 mm. pressure. It reacts with nitrous acid, forming a *nitroso*-derivative, $\text{C}_{12}\text{H}_{10}\text{O}_3\text{N}_2$, which crystallises in brownish-red needles and decomposes at 175—180°. The *benzoyl*

derivative, $\text{NHBz} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$, crystallises in slender, colourless needles and melts at $193-194^\circ$. The *formyl* derivative, $\text{COH} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$, crystallises in reddish-white needles and decomposes at $140-150^\circ$.

4-Benzeneazo-8-acetylamino-1-naphthol, $\text{NPh} \cdot \text{N} \cdot \text{C}_{10}\text{H}_5(\text{NHAc}) \cdot \text{OH}$, formed by the action of diazobenzene chloride on 8-acetylamino-1-naphthol in alcoholic solution, crystallises in dark red, glistening needles, melts at $215-216^\circ$, and on reduction with stannous chloride and hydrochloric acid yields 4:8-diamino-1-naphthol. This forms a *diacetyl* derivative, $\text{C}_{14}\text{H}_{14}\text{O}_3\text{N}_2 \cdot \text{H}_2\text{O}$, crystallising in white needles and melting at 247° , and a *triacetyl* derivative, $\text{OAc} \cdot \text{C}_{10}\text{H}_5(\text{NHAc})_2$, crystallising in stellate groups of small, white needles and melting at 258° .

The action of bromine on 8-acetylamino-1-naphthol in hot glacial acetic acid solution leads to the formation of *tribromo-2-methylnaphth-peri-oxazole dibromide*, $\text{C}_{10}\text{H}_3\text{Br}_3 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{CMe, Br}_2$, which crystallises from benzene in shining, yellow, matted, slender needles, melts at 235° , is stable towards alkali hydroxides and acids, and, when reduced with stannous chloride and hydrochloric acid in boiling glacial acetic acid solution, yields *tribromo-2-methylnaphth-peri-oxazole*, $\text{C}_{11}\text{H}_3\text{OBr}_3\text{Me}$; this crystallises in colourless needles, melts at 215° , is insoluble in aqueous alkali hydroxides, and forms the yellow dibromide when treated with bromine in glacial acetic acid solution.

Tribromo-2-phenylnaphth-peri-oxazole, $\text{C}_{10}\text{H}_3\text{Br}_3 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{CPh}$, prepared by the action of bromine on 8-benzoylamino-1-naphthol in hot glacial acetic acid solution, crystallises in slender, glistening needles, melts at 234° , and is highly stable.

8-Acetylamino-1-naphthyl acetate, $\text{NHAc} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OAc}$, formed by boiling 8-amino-1-naphthol hydrochloride with sodium acetate and acetic anhydride, crystallises in white needles, melts at 118.5° , decomposes slightly when distilled under reduced pressure, and when boiled with dilute sodium hydroxide yields 8-acetylamino-1-naphthol. With bromine in glacial acetic acid solution at the ordinary temperature, it forms a *monobromo-derivative*, $\text{C}_{14}\text{H}_{12}\text{O}_3\text{NBr}$, melting at 203° , but when boiled with an excess of bromine in glacial acetic acid solution yields *tribromo-2-methylnaphth-peri-oxazole dibromide*.

8-Benzoylamino-1-naphthyl benzoate, $\text{C}_{24}\text{H}_{17}\text{O}_3\text{N}$, formed by heating 8-amino-1-naphthol hydrochloride with sodium acetate and an excess of benzoic anhydride, crystallises in large, white needles and melts at $206-207^\circ$.

5-Nitro-8-acetylamino-1-naphthyl acetate, $\text{NO}_2 \cdot \text{C}_{10}\text{H}_5(\text{NHAc}) \cdot \text{OAc}$, prepared by adding 8-acetylamino-1-naphthyl acetate to an excess of ice-cooled nitric acid of sp. gr. 1.38, crystallises from alcohol in long, light yellow, glistening needles, melts at 224° , and is hydrolysed by boiling dilute sodium hydroxide, yielding 5-nitro-8-acetylamino-1-naphthol, $\text{NO}_2 \cdot \text{C}_{10}\text{H}_5(\text{NHAc}) \cdot \text{OH}$; this crystallises in red needles, melts at 192° , and dissolves in dilute alkali hydroxides, forming a red solution. It couples with diazonium salts in alkaline solution and on reduction with stannous chloride and hydrochloride yields an easily oxidisable diamino-1-naphthol.

8-Acetyl-amino-1-methoxynaphthalene, $\text{NHAc} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OMe}$, prepared by the action of methyl sulphate on 8-acetyl-amino-1-naphthol, crystallises in silvery-white needles, melts at 128° , boils at $138\text{--}140^\circ$ under 14 mm. pressure, and forms a *monobromo*-derivative, $\text{C}_{13}\text{H}_{12}\text{O}_2\text{NBr}$, melting at 124° . When boiled with dilute hydrochloric acid, the acetyl-amino-methyl ether yields the *hydrochloride* of 8-amino-1-methoxynaphthalene, $\text{C}_{11}\text{H}_{11}\text{ON} \cdot \text{HCl}$, which crystallises from alcohol; the *picrate*, $\text{C}_{11}\text{H}_{11}\text{ON} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, crystallises in greenish-yellow needles and melts at 172° . The free *base*, $\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OMe}$, is an oil which boils at $180\text{--}185^\circ$ under 14 mm. pressure, and rapidly darkens. When diazotised and coupled with β -naphthol in sodium carbonate solution, it forms an *azo*-compound, $\text{C}_{21}\text{H}_{16}\text{O}_2\text{N}_2$, which crystallises from benzene in dark violet-red, metallic, hexagonal plates and melts at 177° . When boiled in sulphuric acid solution, the diazonium salt obtained from 8-amino-1-methoxynaphthalene yields the *monomethyl ether* of 1:8-dihydroxynaphthalene; the *picrate*, $\text{C}_{11}\text{H}_{10}\text{O}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, melts at 173° .

When diazotised in well-cooled dilute solution and boiled with dilute sulphuric acid, 8-amino-1-naphthol yields α -naphthol. The action of nitrous acid on 8-amino-1-naphthol in concentrated solution leads to the formation of 2-nitroso-8-amino-1-naphthol *hydrochloride*, $\text{OH} \cdot \text{C}_{10}\text{H}_5(\text{NO}) \cdot \text{NH}_2 \cdot \text{HCl}$, which crystallises in green needles, melts at 250° , and forms a violet coloration with aqueous sodium hydroxide. The concentrated strongly acid solution of the diazonium salt formed together with the nitroso-derivative is reduced by stannous chloride and hydrochloric acid to 2:8-diamino-1-naphthol *hydrochloride*; this crystallises in white needles and forms a *benzylidene* derivative, $\text{CHPh} \cdot \text{N} \cdot \text{C}_{10}\text{H}_5(\text{NH}_2) \cdot \text{OH}$, which separates from alcohol in yellow needles. The *triacetyl* derivative, $\text{C}_{16}\text{H}_{16}\text{O}_4\text{N}_2$, forms white, slender needles and melts at 234° .
G. Y.

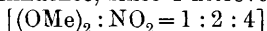
Reduction of Aromatic Sulpho-acids to Mercaptans by Alkali Hydrosulphides. CARL SCHWALBE (*Ber.*, 1906, 39, 3102—3105).—Sodium naphthalene- β -sulphonate and a 50 per cent. solution of potassium hydrosulphide are heated for three hours at $200\text{--}220^\circ$ under a pressure of 10—12 atm. in an iron vessel. The precipitate obtained by heating the product with dilute hydrochloric acid is treated with ether, whereby β -naphthol and the mercaptan are extracted, whilst the disulphide remains undissolved and can be converted into the mercaptan by heating with potassium hydrosulphide and alcohol. The mercaptan yields dyes with diazo-compounds.

Benzene-sulphonic acid and *m*-disulphonic acid yield coloured products, from which liquids can be obtained having the odour of mercaptans.

Primuline and thioflavin yield dyes containing sulphur. C. S.

Distribution of Auxochromes in the Molecule. HUGO KAUFFMANN and W. FRANCK (*Ber.*, 1906, 39, 2722—2726).—The production of colour in a compound containing two or more auxochromes depends not so much on the relative positions of the auxochrome and

chromophore as on the relative positions of the auxochromes themselves. The effect appears to be most pronounced when the two auxochromes are in the para-position, as, for example, in nitroquinol dimethyl ether; the effect is less when they are in the ortho-position, and is practically nil when in the meta-position; thus the ethers of 2- and of 4-nitroresorcinol are nearly colourless. The position of the chromophore is also of influence, since 4-nitroveratrole



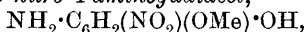
is pale yellow, and the isomeric 3-nitro-compound, colourless. The effect of the positions of the auxochromes is seen by a comparison of 3-nitroveratrole and nitroquinol dimethyl ether.

2-Nitroresorcinol dimethyl ether, obtained by the action of methyl sulphate on 2-nitroresorcinol in the presence of sodium hydrogen carbonate, crystallises from acetic acid in colourless needles, melting at 129–130°.

4-Nitroresorcinol diethyl ether melts at 85°, and the isomeric 2-nitro-compound at 106–107°. J. J. S.

3:4-Diaminoguaiacol. FRITZ FICHTER and JULIUS SCHWAB (*Ber.*, 1906, 39, 3339–3341. Compare Rupe, *Abstr.*, 1898, i, 72).—4-Acetylaminoguaiacyl acetate, $\text{C}_{11}\text{H}_{13}\text{O}_4\text{N}$, prepared from 4-amino-guaiacol, crystallises from water in silvery scales, melts at 149°, and when boiled with aqueous sodium carbonate yields 4-acetylaminoguaiacol, $\text{C}_9\text{H}_{11}\text{O}_3\text{N}$, melting at 118°.

3-Nitro-4-acetylaminoguaiacyl acetate, $\text{C}_{11}\text{H}_{12}\text{O}_6\text{N}_2$, prepared by the action of ice-cooled concentrated nitric acid on 4-acetylaminoguaiacyl acetate, crystallises from water or alcohol in yellow, rhombic plates or needles, melts at 158°, and on hydrolysis yields 3-nitro-4-acetylaminoguaiacol, $\text{C}_8\text{H}_{10}\text{O}_5\text{N}_2$, crystallising in orange-red prisms and melting at 223°, together with 3-nitro-4-aminoguaiacol,

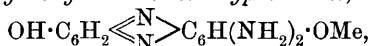


crystallising from benzene or water in light red needles and melting at 169–171°.

3-Nitro-4-benzoylaminoguaiacyl benzoate, $\text{C}_{21}\text{H}_{16}\text{O}_6\text{N}_2$, crystallises in yellow, glistening needles and melts at 177°.

Reduction of 3-nitro-4-acetylaminoguaiacyl acetate with stannous chloride and hydrochloric acid leads to the formation of the hydrochloride of 3:4-diaminoguaiacol, which is readily oxidised, and condenses with benzil in alcoholic solution in presence of sodium acetate, forming 7-hydroxy-8-methoxy-2:3-diphenylquinoxaline, $\text{C}_{21}\text{H}_{16}\text{O}_2\text{N}_2$, crystallising in brownish-red, metallic needles and melting at 235°.

2:3-Diamino-8-hydroxy-1:9-dimethoxyphenazine,



is formed by passing a current of air through an aqueous solution of 3:4-diaminoguaiacol hydrochloride in presence of ammonia; it crystallises in glistening scales or almost black, glistening needles, gives with concentrated sulphuric acid a green coloration, becoming blue, violet, and finally red on dilution, dissolves in alcohol, forming a brown solution with green fluorescence, and dyes animal and vegetable fibres a brownish-red. G. Y.

Constitution of Guaiacolmonosulphonic Acids and of a Mononitroguaiacol. LUDWIG PAUL (*Ber.*, 1906, **39**, 2773—2782).—*Potassium veratrolesulphonate* crystallises in colourless needles with $1\frac{1}{2}\text{H}_2\text{O}$ and melts and decomposes at about 300° ; identical preparations are obtained either by sulphonating veratrole or by methylating Heyden's *o*- or *p*-guaiacolsulphonic acids (D.R.-P. 13820). *Veratrolesulphonic chloride* crystallises from ether in needles melting at 76° ; the *amide* forms colourless needles melting at 136° . 5-Nitroguaiacol, prepared either by the action of fuming nitric acid on acetylguaiacol or by diazotising Cahours' (*Annalen*, 1850, **74**, 301) 4-nitro-*o*-anisidine, crystallises in needles and melts at 104° . Its constitution is confirmed by the conversion into Wisinger's β -nitrocatechol methyl ethyl ether (*Abstr.*, 1902, **i**, 205), and the reduction of this to 4-methoxy-3-ethoxybenzenesulphonic acid, identified by means of its chloride and amides; the latter compound was also obtained from Heyden's *o*-guaiacolsulphonic acid, his *p*-guaiacolsulphonic acid yielding 3-methoxy-4-ethoxybenzenesulphonic acid, of which the *chloride* crystallises in yellow needles and melts at 72° , and the *amide* forms white needles melting at 192° .

E. F. A.

Behaviour of Cholesterol to Light. II. ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1906, **48**, 546—548. Compare *Abstr.*, 1905, **i**, 128).—The changes previously described as occurring in cholesterol as the result of the action of light take place similarly in *ischolesterol* from sheep's wool-fat, in *phytosterol* from wheat grains, and in *ergosterol* from the fungus *Boletus edulis*. The changes do not occur in sealed tubes in which the air has been displaced by carbon dioxide, and are therefore probably due to oxidation taking place on exposure to sunlight.

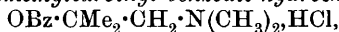
W. D. H.

Arnidiol Phenylurethane. TIMOTHÉE KLOBB (*Bull. Soc. chim.*, 1906, [iii], **35**, 741—744. Compare *Abstr.*, 1905, **i**, 594, and Bloch, *Abstr.*, 1904, **i**, 236).—When heated at 150 — 180° with ammonia solution in a closed tube, the phenylurethane yields arnidiol, aniline, and carbon dioxide, and when heated alone at 250 — 300° for two hours in a closed tube it furnishes aniline, carbon dioxide, and a hydrocarbon, *arnidiene*, $\text{C}_{28}\text{H}_{42}$. The latter crystallises from ether in needles, melts at 234 — 236° , and then sublimes. It gives colour reactions similar to those of arnidiol.

T. A. H.

Preparation of Aminoalkyl Esters. J. D. RIEDEL (D.R.-P. 169787. Compare this vol., **i**, 631).—The aminoalkyl esters having the general formula $\text{NRR}'\cdot\text{CH}_2\cdot\text{CR}''\text{R}'''\cdot\text{O}\cdot\text{X}$, where R, R', R'', and R''' are aryl or alkyl groups and X is an acyl group, are of great importance therapeutically, because they have the property of producing local anæsthesia without being poisonous; this physiological action seems to depend on the presence in the molecule of a secondary or tertiary amino-group and a tertiary alcohol group, which has been esterified with some suitable aromatic acid.

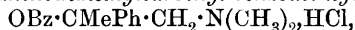
Dimethylaminotrimethylcarbinyl benzoate hydrochloride,



results from the interaction of dimethylaminotrimethylcarbinol and

benzoyl chloride in benzene solution; it crystallises from alcohol in transparent cubes, soluble in water and melting at 202° .

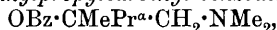
Phenyl dimethylaminodimethylcarbinyl benzoate hydrochloride,



obtained from phenyldimethylaminodimethylcarbinol by the Schotten Baumann reaction, crystallises from alcohol in plates, melts at 206° , and is readily soluble in water.

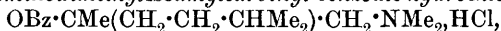
Dimethylaminodimethylethylcarbinyl benzoate, an oil boiling at 149° under 25 mm. pressure, yields a *hydrochloride* crystallising in needles or leaflets and melting at 175° and an *oxalate* which separates in fine needles and melts at 145° .

Dimethylaminodimethylpropylcarbinyl benzoate hydrochloride,



crystallises from alcohol or ether in small, hygroscopic needles melting at 146° .

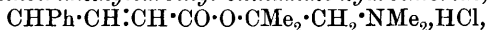
Dimethylaminodimethylisoamylcarbinyl benzoate hydrochloride,



crystallises from ether-alcohol in silky needles melting at 138° ; it is very soluble in water and insoluble in boiling acetone; its taste is bitter and acrid. The platinichloride melts at 178° .

The *hydrochlorides* of *dimethylaminomethyldiethylcarbinyl* and *benzyl-dimethylaminodimethylcarbinyl benzoates* are well-defined crystalline salts melting respectively at 189° and 195° .

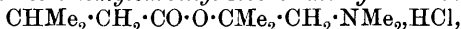
Dimethylaminotrimethylcarbinyl cinnamate hydrochloride,



prepared by the interaction of dimethylaminotrimethylcarbinol and cinnamyl chloride in benzene solution, separates in large, tabular crystals which dissolve in acetone and are moderately soluble in hot alcohol, but much less soluble in the cold solvent; it melts at 208° .

The cinnamyl derivatives of the other aminoalcohols were similarly prepared, and all yielded well-defined crystalline hydrochlorides with definite melting points.

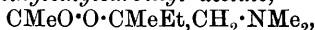
Dimethylaminotrimethylcarbinyl isovalerate hydrochloride,



obtained by employing isovaleryl chloride instead of cinnamyl chloride in the preceding preparation, separates in large leaflets which are greasy to the touch and have a bitter taste; it is readily soluble in the ordinary solvents except cold ether and petroleum; it melts indefinitely at 112° .

Dimethylaminodimethylethylcarbinyl diethylcarbamate hydrochloride, $\text{NEt}_2 \cdot \text{CO} \cdot \text{O} \cdot \text{CMeEt} \cdot \text{CH}_2 \cdot \text{NMe}_2 \cdot \text{HCl}$, was prepared by heating for one day on the water-bath equivalent quantities of dimethylaminodimethylethylcarbinol and diethylcarbamyl chloride, $\text{NEt}_2 \cdot \text{COCl}$; when recrystallised from ether alcohol it separates in lustrous needles or leaflets and decomposes at 144° .

Dimethylaminodimethylethylcarbinyl acetate,



was produced by heating the corresponding carbinol with acetic anhydride for four hours at 120° ; it boils at $80-85^{\circ}$ under 32 mm. pressure and rapidly darkens and decomposes on exposure to light.

G. T. M.

Preparation of the Alkali Salts of Organic Acids from the Corresponding Nitriles and Amides. DEUTSCHE GOLD- UND SILBERSCHEIDE-ANSTALT VORM. RÜSSLER (D.R.-P. 169186).—The organic nitriles or amides are hydrolysed by a mixture of equivalent quantities of calcium hydroxide and some alkali salt, such as the carbonate or oxalate, which is capable of forming a sparingly soluble calcium salt, the alkali salt of the organic acid being subsequently obtained by evaporating the filtrate. The process is applicable in the following cases: phenylaminoacetonitrile, acetonitrile, benzonitrile, acetamide, and benzamide. G. T. M.

Alkylation and Arylation of Anthranilic Acid. JOSEF HOUBEN and WALTER BRASSERT (*Ber.*, 1906, 39, 3233—3240).—Willstätter and Kahn's method (*Abstr.*, 1904, i, 235) for alkylating anthranilic acid was modified by conducting the alkylation with methyl sulphate in glacial acetic acid solution. When a mixture of anthranilic acid, sodium carbonate, water, and methyl sulphate is boiled, methyl methylanthranilate is formed in addition to methylanthranilic acid.

Whilst a mixture of methylanthranilic acid, dimethylanthranilic acid, and methyl anthranilate is produced by boiling together anthranilic acid, methyl iodide, and aqueous potassium hydroxide according to H. Meyer's method, it is possible to obtain methylanthranilic acid in good yield if an excess of alkali is avoided.

Anthranilic acid may also be methylated by boiling it with methyl sulphate and water. Although in the special case of anthranilic acid the yield of the methylated acid is not as good as that from other methods, the results with *m*- and *p*-aminobenzoic acids are good, and the method is recommended for the methylation of substances which are sensitive towards alkalis.

Anthranilic acid may be ethylated either by H. Meyer's method or by ethyl sulphate. Ethyl bromide is a convenient substitute for ethyl iodide when Meyer's method is used.

Benzylanthranilic acid was obtained by boiling together anthranilic acid, water, potassium carbonate, and benzyl chloride. *p*-Nitrobenzylanthranilic acid may be prepared in a similar manner.

Phenylanthranilic acid was obtained by heating a mixture of anthranilic acid, copper, bromobenzene, sodium carbonate, and water (compare Goldberg, this vol., i, 426).

α -Naphthylanthranilic acid was obtained by heating a mixture of anthranilic acid, sodium carbonate, water, copper, and α -naphthyl bromide.

Allyl chloride differs from propyl and isobutyl chlorides by reacting readily with anthranilic acid and aqueous potassium carbonate to form allylanthranilic acid. A. McK.

Preparation of the Alkamine Esters of *o*- and *m*-Aminobenzoic Acids. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 170587, 172301).—The *o*-nitrobenzoyl ester of diethylaminoethanol is an oil produced by condensing *o*-nitrobenzoyl chloride and diethylaminoethanol in benzene solutions; on reduction it yields an

oily *o*-aminobenzoyl ester, the *monohydrochloride* of which separates from alcohol in colourless crystals and melts at 125—127°.

The *m*-compound can be prepared either in the preceding manner or as follows. Methyl *m*-aminobenzoate was heated for twelve hours with diethylaminoethanol and the excess of the latter removed by distillation under reduced pressure; the product was rendered neutral with hydrochloric acid, in which it dissolved. The solution, after extraction with ether to remove the unaltered methyl *m*-aminobenzoate, was concentrated to obtain *m*-aminobenzoyldiethylaminoethanol hydrochloride, which, when recrystallised from alcohol, separated in colourless prisms melting at 118—120°. The base set free by alkalis solidifies on cooling, and after crystallisation from light petroleum melts at 45—47°.

m-Aminobenzoyl- α -hydroxyethylpiperidine was prepared either by heating ethyl *m*-aminobenzoate and α -hydroxyethylpiperidine or by mixing α -hydroxyethylpiperidine and *m*-aminobenzoic acid with cold concentrated sulphuric acid and then warming the mixture on the water-bath. In both cases the base was purified by means of its monohydrochloride, then set free by alkalis and recrystallised from light petroleum, when it melted at 73—74°.

Chloroethyl m-aminobenzoate, obtained either by esterifying *m*-aminobenzoic acid with ethylene chlorohydrin, or by reducing *m*-nitrobenzoyl ethylene chlorohydrin, was heated with diethylamine at 100—120°. The oily *m*-aminobenzoate of diethylaminoethanol solidified on cooling and was purified by conversion into its monohydrochloride, which crystallised from alcohol in colourless prisms and melted at 118—120°.

The hitherto unknown alkamine esters of the *o*- and *m*-azobenzoic acids are prepared by heating the alkyl azobenzoates with the alkamines; the oily or crystalline products, which are red when reduced with stannous chloride or tin and hydrochloric acid, yield the corresponding alkamine esters of the aminobenzoic acids. Thus *m*-azobenzoylpiperidoethanol, which separates in orange-red crystals melting at 72—74°, furnishes *m*-aminobenzoylpiperidoethanol, melting at 79—80° and yielding a hydrochloride melting at 187—189°.

o-Aminobenzoyldiethylaminoethanol is prepared similarly; it is oily and forms a crystalline hydrochloride melting at 125—126°.

m-Aminobenzoyldiethylaminoethanol melts at 45—47°; and its hydrochloride at 118—120°.

G. T. M.

Preparation of *N*-Alkylated Alkamine Esters of *o*- and *m*-Aminobenzoic Acids. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 172447. Compare preceding abstract).—*N*-Dimethylantranilic acid and diethylaminoethanol when condensed in concentrated sulphuric acid, first at 0° and then on the water-bath, give rise to an oily alkamine ester, the hydrochloride of which melts at 135—137°.

N-Ethylantranilic acid and hydroxyethylpiperidine, when similarly condensed, yield an oily alkamine ester, the hydrated hydrochloride of which melts at 106—108°, whilst the dehydrated substance melts at 142—145°.

The alkamine ester, from *m*-dimethylaminobenzoic acid and diethyl-

aminoethanol, is an oil, giving rise to a crystalline hydrochloride melting at 187°. G. T. M.

Preparation of the Alkamine Esters of *p*-Aminobenzoic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 172568).—The alkamine esters of *p*-aminobenzoic acid may be prepared by heating the alkyl esters of this acid with an alkamine at the boiling point of the latter, the condensation being accompanied by the elimination of alcohol. The *p*-aminobenzoate of hydroxyethylpiperidine is obtained in the form of its crystalline hydrochloride by heating ethyl *p*-aminobenzoate with hydroxyethylpiperidine at 200–210° for four to six hours, distilling off the excess of alkamine under reduced pressure, neutralising the residue with dilute hydrochloric acid, filtering off unaltered ethyl *p*-aminobenzoate, and concentrating the filtrate. The alkamine ester itself was set free by alkalis as an oil which soon solidified; after crystallisation from light petroleum, the ester was obtained in colourless needles melting at 90°.

The alkamine ester from *p*-dimethylaminobenzoic acid and hydroxyethylpiperidine, when crystallised from light petroleum, melts at 38–40°. The corresponding ester from hydroxyethyldiethylamine melted at 59–60°. Both these esters form crystallisable hydrochlorides.

The esters may be employed in therapeutics as local anaesthetics.

G. T. M.

Carbithionic Acids. I. Arylcarbithionic Acids. JOSEF HOUBEN [with HEINRICH POHL] (*Ber.*, 1906, 39, 3219–3233. Compare Houben and Kesselkaul, *Abstr.*, 1903, i, 42).—*Phenylcarbithionic acid* (dithiobenzoic acid), $C_6H_5 \cdot CS \cdot SH$, prepared by the action of magnesium phenyl bromide (1 mol.) on carbon disulphide (1 mol.), is a reddish-violet, pungent oil. Its ethereal solution is carmine-red. Its lead salt separates from toluene in purple leaflets or needles and melts at 204.5° (corr.). Its zinc salt is a yellow, amorphous solid and begins to decompose at about 100°. Its mercury salt separates from benzene in leaflets with a bronze lustre and melts at 150°.

Thiobenzoyl disulphide, $S_2(CSPh)_2$, prepared by the addition of a solution of iodine in potassium iodide to sodium dithiobenzoate, is a crystalline solid and melts at 92.5°.

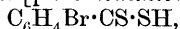
Details are given for the preparation of *benzylcarbithionic acid* (dithiophenylacetic acid, $CH_2Ph \cdot CS_2H$ (compare Houben and Kesselkaul, *loc. cit.*). The lead salt separates from benzene in yellow needles and melts at 149°. The zinc salt crystallises from benzene in yellow leaflets and melts at 221°.

Thiophenylacetyl disulphide, $S_2(CS \cdot CH_2Ph)_2$, prepared by the action of a solution of iodine in potassium iodide on sodium dithiophenylacetate, melts at 78°.

α -Naphthylcarbithionic acid (α -dithionaphthoic acid), $C_{10}H_7 \cdot CS \cdot SH$, prepared from magnesium α -naphthyl bromide and carbon disulphide, is a dark red oil. Its lead salt separates from benzene in needles; its zinc salt is a yellow solid; its iron salt, $(C_{10}H_7 \cdot CS_2)_3Fe$, separates from ether in green leaflets.

α-Thionaphthoyl disulphide, $S_2(CS \cdot C_{10}H_7)_2$, prepared by the action of a solution of iodine in potassium iodide on sodium *α*-naphthylcarbithionate, melts at 169°. Its solution in concentrated sulphuric acid assumes a dark blue shade, which disappears on the addition of water. It is oxidised to *α*-naphthoic acid by concentrated nitric acid.

p-Bromophenylcarbithionic [*p*-bromodithiobenzoic] acid,



prepared by the action of magnesium *p*-dibromophenyl on carbon disulphide, is a brownish-red oil. Its lead salt may be crystallised from benzene or toluene; its zinc salt is a yellow, amorphous powder; its iron salt is a dark green powder. A. McK.

Action of Acetyl Bromide on Benzyl Cyanide. FRANZ KUNCKELL [with F. FLOS] (*Ber.*, 1906, 39, 3145—3146).—*p*-Acetylbenzylcyanide [*p*-acetylphenylacetoneitrile], $C_6H_4Ac \cdot CH_2 \cdot CN$, prepared by the addition of aluminium chloride to a mixture of phenylacetoneitrile, acetyl bromide, and carbon disulphide, separates from a mixture of benzene and light petroleum in white needles, melts at 83—84°, and boils with slight decomposition at 333—334°. Its *hydrazone* melts at 112—114°. Its *oxime* separates from benzene in cubes and melts at 123°.

m-Acetylphenylacetoneitrile, obtained as a by-product in the preceding reaction, is a yellow oil which boils at 327—331° and has the sp. gr. 1.109 at 23°. When oxidised by permanganate, it yields *isophthalic acid*. A. McK.

Action of Nascent Hypoiodous Acid on Acids containing an Ethylenic Linking. Iodo-lactones. J. BOUGAULT (*Compt. rend.*, 1906, 143, 398—400. Compare Abstr., 1905, i, 9).—Acids of the type $CHR:CH \cdot CH:CH \cdot CO_2H$ (sorbic, piperic, or cinnamylacrylic acid), although containing an ethylenic linking in the $\gamma\delta$ -position, do not react with iodine and yellow mercuric oxide or iodine and alkali carbonates (nascent hypoiodous acid), but cinnamylisocrotonic acid (this vol., i, 671) yields the iodo-lactone, $CHPh:CH \cdot CH \begin{smallmatrix} \swarrow CHI \cdot CH_2 \\ \searrow O - CO \end{smallmatrix}$.

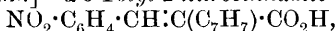
α-Ketonic acids of the type $CHR:CH \cdot CO \cdot CO_2H$ (benzylidene-, piperylidene-, cinnamylidene-, or furfurylidene-pyruvic acid) do not form iodo-lactones by the action of nascent hypoiodous acid, but the corresponding *α*-hydroxy-acids, $CHR:CH \cdot CH(OH) \cdot CO_2H$, obtained by the reducing action of sodium amalgam, readily yield iodo-lactones. Neither *β*-benzylidenelævulic acid nor cinnamylparaconic acid forms an iodo-lactone, although each contains an ethylenic linking in the *βγ*-position. M. A. W.

Syntheses and Properties of some New Phenanthrene Derivatives. ROBERT PSCHORR (*Ber.*, 1906, 39, 3106—3124. Compare Abstr., 1896, i, 303; 1900, i, 232, 233, 487, 488, 489; 1902, i, 96; 1903, i, 167).—[With H. TAPPEN].—*α*-*o*-Tolyl-2-nitro-3:4-dimethoxycinnamic acid, $NO_2 \cdot C_6H_2(OMe)_2 \cdot CH:C(C_7H_7) \cdot CO_2H$, resulting from the condensation of sodium *o*-tolylacetate (compare Radziszewski and Wispek, Abstr., 1885, 889), *vic*-*o*-nitrovanillin methyl ether (Abstr., 1899, i, 178), and acetic anhydride at 100°,

forms slender needles and melts at 255° (corr.). The corresponding *amino-acid*, obtained by reduction with ferrous sulphate and ammonium hydroxide, separates from alcohol in yellow prisms and melts at 192° (corr.). The *diazonium chloride*, $C_{18}H_{18}O_4N_2Cl$, precipitated from alcoholic solution by ether, forms yellow prisms and melts and decomposes at $101-102^{\circ}$.

3:4-Dimethoxy-8-methylphenanthrene-9-carboxylic acid, $C_{18}H_{16}O_4$, prepared by warming the diazonium chloride and aqueous sodium carbonate, melts at $178-180^{\circ}$ (corr.), and by distillation under 160 mm. pressure yields 3:4-dimethoxy-8-methylphenanthrene, $C_{17}H_{16}O_2$, which melts at 68° .

[With R. HOFMANN.]— α -o-Tolyl-2-nitrocinnamic acid,



obtained from *o*-nitrobenzaldehyde, acetic anhydride, and sodium *o*-tolylacetate at 100° , melts at 168° (corr.), and by reduction yields the *amino-acid*, $C_{16}H_{15}O_2N$, which occurs in two modifications. It separates from alcohol in yellow, hexagonal prisms which melt at 225° (corr.), whereas a colourless form is precipitated by acidifying the cold ammoniacal solution of the acid. The latter changes into the yellow modification at 170° or in contact with water free from acid.

8-Methylphenanthrene-9-carboxylic acid, $C_{16}H_{12}O_2$, is obtained when the diazotised acid in dilute sulphuric acid is treated with copper powder; it crystallises in flat needles, sinters at 177° , and melts at $181-182^{\circ}$ (corr.). By distillation under 160 mm. pressure it yields 1-methylphenanthrene, $C_{15}H_{12}$, which melts at 123° (corr.) and forms a *picrate*, $C_{15}H_{12} \cdot C_6H_3O_7N_3$, melting at 139° (corr.).

1-Methylphenanthrene is quite stable to potassium permanganate, but by potassium dichromate and sulphuric acid is oxidised to 1-methylphenanthraquinone, $C_{15}H_{10}O_2$, which forms red leaflets and melts at 196° (corr.).

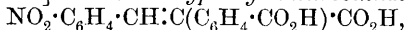
[With F. QUADE.]— α -p-Tolyl-2-nitrocinnamic acid, obtained in a similar manner to the preceding isomeride, melts at 204° (corr.). 5-Nitro-8-methylstilbene, $C_{15}H_{13}O_2N$, occurring as a by-product, forms red prisms and melts at 211° (corr.). The *amino-acid*, $C_{16}H_{15}O_2N$, forms colourless needles, and melts at 206° (corr.). After diazotisation, treatment with copper powder in acid solution or warming with aqueous sodium carbonate produces 6-methylphenanthrene-9-carboxylic acid in 20 per cent. yield. A 70 per cent. yield is obtained by diazotising with amyl nitrite in alcoholic hydrogen chloride solution, diluting with water, and adding copper powder. The acid separates from glacial acetic acid in aggregates of light yellow needles, melts at 238° (corr.), and by distillation at the ordinary pressure yields 3-methylphenanthrene, which melts at 65° , crystallises in long prisms, forms a *dibromide* melting at $86-87^{\circ}$, and a *picrate* which melts at 141° (corr.).

α -p-Tolyl-2-nitro-3:4-dimethoxycinnamic acid, $C_{18}H_{17}O_6N$, melts at 245° (corr.); the corresponding *amino-acid*, $C_{18}H_{19}O_4N$, at 203° (corr.).

3:4-Dimethoxy-6-methylphenanthrene-9-carboxylic acid, $C_{18}H_{16}O_4$, forms hexagonal plates, melts at 253° (corr.), and by distillation in a vacuum yields 3:4-dimethoxy-6-methylphenanthrene, $C_{17}H_{16}O_2$, which

melts at 70—72°, forms a *dibromide*, $C_{17}H_{16}O_2Br_2$, melting at 126—127°, and a *picrate*, melting at 118—119°.

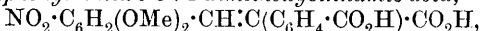
[With H. TAPPEN.]—*α-o-Carboxyphenyl-2-nitrocinnamic acid*,



obtained from sodium homophthalate, melts at 229° (corr.), and by reduction yields the *amino-acid*, $C_{16}H_{13}O_4N$, which forms slender needles and melts at 255—256° (corr.).

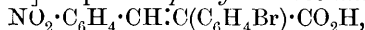
By warming the solution of the diazotised acid, a mixture of phenanthrene-8:9-dicarboxylic acid and its *anhydride* is obtained, which is converted wholly into the latter by crystallisation from glacial acetic acid. It forms glistening needles, melts at 283—284° (corr.), and with ammonia yields the *imide*, $C_{16}H_9O_2N$, which sublimes in elongated crystals and melts at 308—309° (corr.). The pure acid has not been obtained.

α-o-Carboxyphenyl-2-nitro-3:4-dimethoxycinnamic acid,



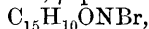
forms yellow needles and melts and decomposes at 259—260° (corr.). The *anhydride*, $C_{18}H_{13}O_7N$, also obtained in the condensation, melts at 217° (corr.). The *amino-acid* is obtained readily, but not crystallised, owing to the formation of the anhydride. When the diazotised acid is warmed, 3:4 dimethoxyphenanthrene-8:9-dicarboxylic acid and its *anhydride*, $C_{18}H_{12}O_5$, are obtained. By crystallisation, from glacial acetic acid, the mixture is converted entirely into the anhydride, which forms yellow needles and melts at 283—284° (corr.).

[With M. SCHÜTZ.]—*α-p-Bromophenyl-2-nitrocinnamic acid*,



obtained from sodium *p*-bromophenylacetate (the *amide* of which, C_8H_8ONBr ,

melts at 192—194°), crystallises in yellow needles, melts at 187°, and by reduction yields the *amino-acid*, $C_{15}H_{12}O_2NBr$, which occurs in yellow needles melting at 213°, or in colourless crystals melting at 222—223°. When the *amino-acid* is warmed with acetic anhydride and concentrated sulphuric acid, *β-p-bromophenylcarbostyryl*,



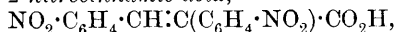
is formed, which melts at 266—267°.

When the acid, dissolved in sodium hydroxide solution, and sodium nitrite, are added to cold dilute sulphuric acid, after some time the diazo-compound separates in yellow flocks. By warming the solution, 3-bromophenanthrene-9-carboxylic acid, $C_{15}H_9O_2Br$, is obtained, which forms yellow needles, melts at 290—291°, evolves hydrogen bromide on distillation, and is oxidised to 3-bromophenanthraquinone (compare Schmidt, Abstr., 1904, i, 1034) by chromic and acetic acids.

[With J. POPOVIC.]—*α-o-Bromophenyl-2-nitro-3:4-dimethoxycinnamic acid*, $NO_2 \cdot C_6H_2(OMe)_2 \cdot CH : C(C_6H_4Br) \cdot CO_2H$, melts at 266—267° (corr.). The *amino-acid*, $C_{17}H_{16}O_4NBr$, forms yellow prisms, melts at 218° (corr.), and after diazotisation with amyl nitrite yields 8-bromo-3:4-dimethoxyphenanthrene-9-carboxylic acid, $C_{17}H_{13}O_4Br$, which separates from hot alcohol in colourless prisms, melts at 228—229° (corr.), and by distillation in a vacuum loses carbon dioxide and hydrogen bromide, yielding a mixture of 8-bromo-3:4-dimethoxyphenanthrene, which melts at 81—82°, and the *lactone* of 8-hydroxy-

3:4-dimethoxyphenanthrene-9-carboxylic acid. The former, which is soluble in ether, is purified in the form of the *picrate*, which melts at 117°. The lactone, which is insoluble in ether, separates from alcohol in slender, yellow needles and melts at 160° (corr.). When its solution in sodium hydroxide is acidified, the acid $C_{17}H_{14}O_5$ is precipitated; it crystallises in long needles and melts at 193° (corr.).

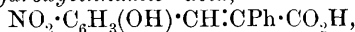
α-o-Nitrophenyl-2-nitrocinnamic acid,



melts at 207° (corr.). The diamino-acid has not been isolated; by acidifying its ammoniacal solution, *α-o-aminophenyl-2-aminocinnamic anhydride* (3-*o*-aminobenzylideneoxindole), $C_{15}H_{12}ON_2$, is obtained, which forms yellow prisms and melts at 233—234° (corr.). By treating the diazonium compound with copper powder, the *anhydride* of 8-aminophenanthrene-9-carboxylic acid, $C_{15}H_9ON$, is obtained; it separates from dilute alcohol in faintly yellow prisms and melts at 231° (corr.).

The condensation of *vic-o*-aminovanillin and sodium *o*-nitrophenylacetate leads to the formation of the *anhydride* of *α-o*-nitrophenyl-2-amino-4-acetoxy-3-methoxycinnamic acid (*o-nitro-4-acetoxy-3-methoxycarboxystyryl*), $C_{18}H_{14}O_6N_2$, which melts at 261° (corr.).

[With F. QUADE.]—The condensation of 2-nitro-5-hydroxybenzaldehyde and sodium phenylacetate leads to the formation of *α-phenyl-2-nitro-5-hydroxycinnamic acid*,



which melts at 219—220°. The *amino-acid*, $C_{13}H_{13}O_3N$, forms yellowish-brown prisms and melts at 237—239° (corr.).

2-Hydroxyphenanthrene-9-carboxylic acid, $C_{15}H_{10}O_3$, melts at 278° (corr.), and the *acetyl* derivative, $C_{17}H_{12}O_4$, at 223° (corr.).

α-Phenyl-2-nitro-3-acetoxycinnamic acid, $C_{17}H_{13}O_6N$, results from the reaction between 2-nitro-3-hydroxybenzaldehyde, sodium phenylacetate, and acetic anhydride; it forms yellow prisms, melts at 254° (corr.), and by reduction and simultaneous hydrolysis yields *α-phenyl-2-amino-3-hydroxycinnamic acid*, $C_{15}H_{13}O_3N$, which separates from dilute methyl alcohol in yellow, rhombic plates, melts at 201° (corr.), and does not form phenanthrene derivatives. C. S.

Electrolytic Reduction of Aromatic Carboxylic Acids. CARL METTLER (*Ber.*, 1906, 39, 2933—2942. Compare *Abstr.*, 1905, i, 436; this vol., i, 497).—The reductions were performed in an apparatus consisting of a porous cell, containing a lead anode and filled with dilute sulphuric acid, placed in a beaker containing a lead electrode and the cathode liquid, generally a solution of the acid to be reduced in 20—30 per cent. alcoholic sulphuric acid. A number of aromatic acids were thus reduced to the corresponding alcohols. 3:5-Dichlorosaligenin, obtained from 3:5-dichlorosalicylic acid, crystallised in needles melting at 82°; 3:5-dibromosaligenin melts at 87—88°. The *ethyl ether* of 3:5-dichloro-p-hydroxybenzyl alcohol melts at 86°. *o*-Diphenyldicarboxylic acid is reduced to phenanthraquinone; phthalic acid and terephthalic acid give the corresponding dihydro-derivatives.

E. F. A.

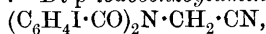
Preparation of Menthyl Salicylate. BERTRAND BIBUS and RUDOLF SCHEUBLE (D.R.-P. 171453. Compare Trans., 1903, **83**, 1213, and 1904, **85**, 1262).—The esterification of menthol is an operation which is effected only with some difficulty owing to the sensitiveness of this alcohol to the action of dehydrating agents, especially when employed at high temperatures. This difficulty is increased when the acid employed also tends to decompose at high temperatures. It has now been found that *menthyl salicylate* may be obtained in fairly good yield (75—80 per cent. of the calculated amount) by heating 30 parts of menthol and 140 parts of salicylic acid at 140—220° in a current of gas such as hydrogen or carbon dioxide. After removing the unchanged acid with aqueous alkali carbonate, the oily residue is fractionated. The ester is a viscid, colourless liquid, having a sweet taste and but very little odour; it is insoluble in water, but dissolves in the ordinary organic solvents. It can only be distilled under diminished pressure, when it boils at 190° and 175° under 15 and 10 mm. pressure respectively. G. T. M.

Preparation of Tyrosine from Silk. EMIL ABDERHALDEN and YUTAKA TERUUCHI (*Zeit. physiol. Chem.*, 1906, **48**, 528—529).—The usual method of preparing tyrosine from proteids, by hydrolysing with boiling 25 per cent. sulphuric acid and removal of the acid with baryta, is tedious, and leads to loss of tyrosine by its inclusion in the precipitate of barium sulphate. The preparation is simplified by the use of fuming hydrochloric acid, evaporating to dryness, and taking up the residue with water. This is again evaporated to dryness and the procedure repeated. After boiling with animal charcoal, the remaining acid is neutralised exactly with sodium hydroxide, when the tyrosine falls out of solution in an almost pure condition. One recrystallisation renders it quite pure. One kilo. of silk yielded 50—65 grams of tyrosine. Cystine may be obtained in a very similar way. W. D. H.

o-, *m*-, and *p*-Iodohippuric Acids. TREAT B. JOHNSON and HAROLD A. MEADE (*Amer. Chem. J.*, 1906, **36**, 294—301).—*o*-Iodohippuric acid, $C_6H_4I \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$, obtained by the action of *o*-iodobenzoyl chloride on aminoacetic acid in presence of sodium hydroxide, crystallises from hot water in clusters of radiating needles and melts at 167°. The *nitrile* separates from alcohol in prisms and melts at 158°. The *ethyl* ester forms irregular prisms and melts at 79—80°.

m-Iodohippuric acid, prepared by warming an aqueous solution of potassium iodide and *m*-diazohippuric acid, crystallises from hot water in thin plates, melts at 155—156°, and is probably identical with the acid obtained by Griess (*Abstr.*, 1871, 702) by the action of hydriodic acid on diazohippuric acid.

p-Iodohippuric acid, obtained by treating aminoacetic acid with *p*-iodobenzoyl chloride, crystallises from hot water in plates and melts at 193°. The *nitrile* separates from alcohol in prismatic crystals and melts at 191—192°. The *ethyl* ester crystallises from alcohol in plates and melts at 128—129°. *Di-p-iodobenzoylaminoacetoneitrile*,



obtained under certain conditions by the action of *p*-iodobenzoyl chloride on aminoacetoneitrile sulphate in presence of sodium hydroxide, crystallises from alcohol in clusters of radiating prisms and melts at 215—216°.

p-Iodobenzoylanilide, $C_6H_4I \cdot CO \cdot NHPh$, melts at 210° . 3:5-Dinitrobenzoylanilide, $C_6H_3(NO_2)_2 \cdot CO \cdot NHPh$, crystallises from alcohol in needles and melts at 234 — 235° . 3:5-Dinitrobenzoyl-*p*-toluidide, $C_6H_3(NO_2)_2 \cdot CO \cdot NH \cdot C_6H_4Me$, does not melt below 280° and is practically insoluble in the usual solvents. 3:5-Dinitrobenzoyl-*o*-toluidide crystallises from alcohol and melts at 241 — 242° .

[With WALTER C. CHALKER.]—3:5-Dinitrobenzoylmethylanilide, $C_6H_3(NO_2)_2 \cdot CO \cdot NPhMe$, separates from alcohol in prismatic crystals, and melts at 155 — 156° . 3:5-Dinitrobenzoyldiphenylamide,

$C_6H_3(NO_2)_2 \cdot CO \cdot NPh_2$, crystallises in prisms and melts at 180 — 181° . 3:5-Dinitrobenzoyl- α -naphthylamide, $C_6H_3(NO_2)_2 \cdot CO \cdot NH \cdot C_{10}H_7$, melts at 268° and is insoluble in the ordinary solvents. E. G.

Decolorisation of a Faintly Alkaline Solution of Phenolphthalein by Alcohol. ROBERT COHN (*Zeit. angew. Chem.*, 1906, 19, 1389—1390).—The decolorisation produced by the addition of alcohol to a faintly alkaline solution of phenolphthalein is attributed to the diminution in the dissociation of the colouring matter. The fact that the colour is restored on warming and disappears again on cooling is explained by assuming that the dissociation varies directly with the temperature. The alcohol employed in these experiments was freshly distilled from alkali in order to ensure absence of acid, and it was demonstrated that the colour changes were not brought about by atmospheric carbon dioxide. P. H.

Preparation of the Amides of Coumarincarboxylic Acid. EMANUEL MERCK (D.R.-P. 172724).—Salicylaldehyde and malonamide were heated until the mixture became solid, when the product, after crystallisation from glacial acetic acid, separated in white, felted needles and melted at 268 — 269° . This substance, coumarincarboxamide, is soluble in methyl and ethyl alcohols and ethyl acetate, but dissolves only sparingly in the other organic solvents.

Coumarincarboxymethylamide, $C_6H_4 \begin{matrix} O-CO \\ | \\ CH:C \cdot CO \cdot NHMe \end{matrix}$, obtained from salicylaldehyde and *s*-malondimethylamide, crystallises from alcohol in long needles melting at 172 — 173° ; it is soluble in chloroform, benzene, or toluene.

Coumarincarboxyanilide, $C_6H_4 \begin{matrix} O-CO \\ | \\ CH:C \cdot CO \cdot NHPh \end{matrix}$, prepared by heating salicylaldehyde and malonanilide, forms long, yellow needles and melts at 250° ; it dissolves readily in the acetone, ethyl acetate, glacial acetic acid, toluene, xylene, and the alcohols, and is only sparingly soluble in benzene, chloroform, light petroleum, or water.

Coumarincarboxymethylanilide, $C_6H_4 \begin{matrix} O-CO \\ | \\ CH:C \cdot CO \cdot NMePh \end{matrix}$, crystallises from dilute alcohol in aggregates of white needles having a green reflex; it melts at 139 — 140° . G. T. M.

Decomposition of Ethyl Terephthalyl diacetate and a Case of Stereoisomerism. LUDWIG BEREND and PAUL HERMS (*J. pr. Chem.*, 1906, [ii], 74, 112—141).—Ethyl terephthalyl diacetate, $C_6H_4(CO \cdot CHAc \cdot CO_2Et)_2$, prepared by gradually adding

sodium ethoxide in absolute alcoholic solution and terephthalyl chloride in ethereal solution to ethyl acetoacetate, forms a white, fine crystalline powder, sinters at 90° , melts at 102.5° , is readily soluble in chloroform, acetone, benzene, ethyl acetate, or aqueous potassium hydroxide, and gives a red coloration with ferric chloride and a bluish-green precipitate with copper acetate. It is converted by the action of 10 per cent. alcoholic ammonia at 60° into acetamide and *ethyl terephthalyl diacetate*, $C_6H_4(CO \cdot CH_2 \cdot CO_2Et)_2$, which crystallises from alcohol in large leaflets, melts at 70° , gives the characteristic colour reaction with ferric chloride, and, when heated with phenylhydrazine in glacial acetic acid solution on the water-bath, yields 3:3'-*p*-phenylenedi-1-phenylpyrazolone, $C_6H_4(C_3N_2H_2OPh)_2$; this melts at 284° , dissolves readily in hot aniline, nitrobenzene, or xylene, is soluble in aqueous sodium hydroxide, gives with copper salts a green, with uranium salts a brownish-red, or with cobalt salts a violet precipitate, and forms an *additive* compound with pyridine, which crystallises in large, white prisms and melts at $284-285^\circ$.

On prolonged boiling with water or very dilute sulphuric acid, ethyl terephthalyl diacetate yields ethyl terephthalyl diacetate and benzoylacetone; hydrolysis with 20 per cent. sulphuric acid leads to the formation of diacetylbenzene or, on prolonged boiling, of acetylbenzoic acid, whilst the products of the hydrolysis with 35 per cent. sulphuric acid are acetylbenzoic and terephthalic acids.

Terephthalyl diacetone, $C_6H_4(CO \cdot CH_2 \cdot COMe)_2$, is formed synthetically by the action of ethyl terephthalate on acetone in presence of sodamide in absolute ethereal solution; it crystallises in silvery leaflets, assumes a green lustre on repeated recrystallisation, and melts at 184° . It reacts with hydrazine hydrate in hot absolute alcoholic solution, forming *p*-phenylenedi-5-methylpyrazole, $C_6H_4(C \begin{smallmatrix} \text{NH} \cdot \text{N} \\ \text{CH} \cdot \text{CMe} \end{smallmatrix})_2$, which crystallises from alcohol in stellate aggregates of needles, or from glacial acetic acid in leaflets, sinters at 327° , and melts and becomes brown at 332° .

Ethyl p-acetylbenzoate, $COMe \cdot C_6H_4 \cdot CO_2Et$, prepared by the action of hydrogen chloride on the corresponding nitrile in absolute alcoholic solution, crystallises from water in white needles, melts at 57° , is sparingly soluble in boiling water, has an aromatic odour in aqueous solution, and is only slowly and incompletely volatile in a current of steam.

p-Diacetylbenzene is obtained in a 95 per cent. yield by boiling ethyl terephthalyl diacetate with 10 per cent. sulphuric acid; the dioxime melts and decomposes at $240-245^\circ$ (compare Ingle, Abstr., 1894, i, 589). *p*-Phenylenedi- α -ethyldiamine [*p*-di- α -amino-diethylbenzene]hydrochloride, $C_6H_4(CHMe \cdot NH_2, HCl)_2$, is prepared by reduction of the dioxime with sodium amalgam in acid solution and treatment of the base with hydrogen chloride in ethereal solution; it does not melt or decompose in a capillary tube at 300° , but decomposes when heated on platinum, and is readily soluble in water or alcohol. The carbamate, $C_6H_4 \begin{smallmatrix} \text{CHMe} \cdot \text{NH} \\ \text{CHMe} \cdot \text{NH}_3 \end{smallmatrix} > CO_2$, formed by passing carbon dioxide into the ethereal solution of the base, melts and decomposes at 85° , is soluble

in water, and is decomposed by acids. *i*-p-Di-*a*-aminodiethylbenzene, $C_{10}H_{16}N_2$, is an oil which has a basic odour, distils without decomposition at about 140° under 12 mm. pressure, solidifies to transparent crystals when strongly cooled, and has $n_D = 1.54126$ at 21.5° . The *d*-tartrate, formed by the action of *d*-tartaric acid on the carbamate, melts and decomposes at 186° , or, after repeated recrystallisations, at 193 – 194° ; the base obtained from the first fraction has $[\alpha]_D - 4.55.8'$ at 22° , that from the last fraction $[\alpha]_D - 5.2.9'$ at 22° . The base obtained from the mother-liquors has $[\alpha]_D + 18.8.8'$ at 22° .

G. Y.

Action of Sodium Hypochlorite on Aldoximes. GIACOMO PONZIO and G. BUSTI (*Atti R. Accad. Sci. Torino*, 1906, **41**, 862–868. Compare this vol., i, 482).—Further study of the action of sodium hypochlorite on the aldoximes shows that the latter, besides yielding peroxides of the form $CHR:N\cdot O\cdot O\cdot N:CHR$, are partially converted into the corresponding azoximes, $\begin{array}{c} CR:N \\ | \\ N=CR \end{array} > O$.

Thus, the interaction of sodium hypochlorite and benzaldoxime gives benzaldoxime peroxide and dibenzylazoxime (compare Beckmann, *Abstr.*, 1889, 980).

m-Nitrobenzaloxime and sodium hypochloride yield: (1) di-*m*-nitrobenzenylazoxime, which melts at 169° ; Stieglitz (*Abstr.*, 1890, 254) gave the melting point as 168° , Krümmel (*Abstr.*, 1895, i, 661) as 138° , Bamberger and Scheutz (*Abstr.*, 1901, i, 548) as 147.5 – 149.5° and Franzen and Zimmermann (this vol., i, 388) as 184° (compare also Minunni and Ciusa, this vol., i, 187). (2) *m*-Nitrobenzaloxime peroxide, melting at 131° ; Minunni and Ciusa (*loc. cit.*) gave the melting point 105° , and Franzen and Zimmermann (*loc. cit.*) 124° .

Anisaloxime and sodium hypochlorite yield: (1) di-*p*-methoxybenzenylazoxime, $OMe\cdot C_6H_4\cdot C \begin{array}{c} N\cdot O \\ \diagup \quad \diagdown \\ N\cdot C \end{array} \cdot C_6H_4\cdot OMe$, which crystallises from alcohol or acetic acid in flattened, shining, white needles melting at 175 – 176° and dissolves readily in chloroform and sparingly in ether. (2) Anisaloxime peroxide (*p*-methoxybenzaloxime peroxide), which melts at 126° ; Franzen and Zimmermann (*loc. cit.*) gave the melting point 119.5° .

Furfuraldoxime peroxide, $O_2(N:CH\cdot C_4H_3O)_2$, prepared by the action of sodium hypochlorite or nitrous acid on furfuraldoxime, crystallises from chloroform in yellow plates which melt and decompose with a slight explosion at 130° . T. H. P.

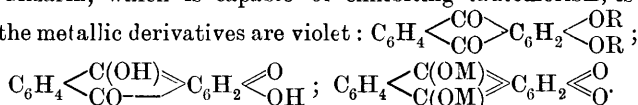
Piperonal and Hydrogen Chloride: a Two-component Three-phase System. FORRIS J. MOORE (*J. Amer. Chem. Soc.*, 1906, **28**, 1188–1190).—When piperonal is treated with dry hydrogen chloride under a pressure of about one atmosphere, the gas is readily absorbed and a liquid additive compound is produced. On reducing the pressure, hydrogen chloride is rapidly evolved from the liquid and crystals of piperonal separate. A rough measurement has shown that the dissociation pressure is about 500 mm.

A description and diagram are given of an apparatus by means of which these changes can be demonstrated as a lecture experiment in illustration of the phase rule. E. G.

Relation between Colour and Constitution of Acids, Salts, and Esters. ARTHUR HANTZSCH (*Ber.*, 1906, 39, 3080—3102).—The term *chromo* is used in preference to *aci*. The prefix *mero* is applied to the names of faintly-coloured hydrogen compounds which consist of solid solutions of the coloured chromo-form in the colourless isomeride. A distinction is drawn between “farbig” and “gefärbt.” The former is applied to substances with specific colour, whilst the latter denotes colourless compounds containing coloured impurities.

Constitutively unchangeable colourless acids produce not only colourless ions, but also colourless ethers, esters, and salts with colourless alkyl or acyl compounds and metals (the oxides of which are colourless) respectively. Constitutively unchangeable coloured acids produce coloured ions, ethers, esters, and salts.

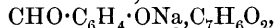
Substances with acidic character are arranged in four classes. (1) Hydrogen, alkyl, acyl, and metallic derivatives are colourless or equally coloured. Such acids are constitutively unchangeable. (2) The hydrogen and alkyl compounds are colourless, whilst the ions and salts exhibit colour. Such substances are pseudo-acids. (3) The hydrogen compound is *coloured*, the alkyl derivatives are colourless, and the ions and salts coloured. In these cases the alkyl compounds are derived from the pseudo-acid, the salts from the real acid, whilst the hydrogen derivative is a *mero*-compound. (4) This class is complicated and has not been examined thoroughly. Change of colour during salt formation is evidence of intramolecular change. Anthraquinone and its non-isomerisable derivatives, alizarin diacetate and dimethyl ether, are yellow, alizarin, which is capable of exhibiting tautomerism, is red, whilst the metallic derivatives are violet:



[With W. PRÄTORIUS and EDITH MORGAN.]—The alkyl and acyl derivatives of the hydroxybenzaldehydes are colourless. The presence of certain nuclear substituents, especially methoxyl or ethoxyl, may confer colour on the hydroxybenzaldehydes.

The salts and ions of *p*-hydroxybenzaldehyde and of its mono- and dibromo-derivatives are colourless. The salts of the meta-isomeride are colourless when solid or in anhydrous solvents, but form yellow aqueous solutions. The *ammonium* salt, $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{ONH}_4$, is obtained from ammonia and the solid at the ordinary temperature, or in ethereal solution at -40° .

Salicylaldehyde yields the following colourless salts: the *acid potassium* salt, $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{OK}, \text{C}_7\text{H}_6\text{O}_2$, by the action of potassium ethoxide ($< \frac{1}{2}$ mol.) on an ethereal solution; the *acid sodium* salt,



in a similar manner with excess of sodium ethoxide. The *ammonium* salt, $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{ONH}_4$, obtained from ammonia and salicylaldehyde,

dissolves in ether, toluene, or light petroleum, melts at 85° . In an atmosphere of ammonia or in alcoholic solution, it changes into hydro-salicylamide. It dissolves in liquid ammonia to an intensely yellow solution of the enolic form, $\text{CH}(\text{ONH}_4) \cdot \text{C}_6\text{H}_4 \cdot \text{O}$, but is recovered colourless after evaporation of the solvent.

Aqueous solutions of these colourless salts are intensely yellow, the colour deepening by warming. The acid sodium salt separates from water or dilute alcohol in yellow leaflets containing $\frac{1}{2}\text{H}_2\text{O}$.

The *potassium* salt, $\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{OK}$, is precipitated from aqueous or alcoholic solution by potassium ethoxide (1 mol.). The *lead*, *mercury*, and *thallium* salts are coloured.

Mono- and di-bromosalicylaldehydes are colourless in non-dissociating solvents, and yellow in water or alcohol. The yellow *ammonium* salt, $\text{O} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH} \cdot \text{ONH}_4$, obtained from ammonia and dibromosalicylaldehyde, solid or in indifferent solvents, can be crystallised from alcohol or ether; when heated it forms a brominated hydrosalicylamide. The *trimethylamine* and *α -piperidine* salts are yellow. Resorcinlaldehyde and phloroglucinolaldehyde yield colourless alkali, and yellow lead, thallium, and mercury salts.

The yellow hydrosalicylamide (m. p. 160°) is a chromo-compound, $\text{N}_2(\text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{OH})_3$. The colourless isomeride, $(\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH})_3\text{N}_2$, resulting from ammonia and the yellow form at -40° , has the same melting point.

[With M. B. BLACKLER.]—The influence of the nature and of the position of substituents on the colour of aromatic hydroxyketones is discussed.

Potassium p-hydroxybenzophenone, $\text{C}_{13}\text{H}_9\text{O}_2\text{K}$, prepared from potassium ethoxide and an ethereal solution of the ketone, contains 1 mol. $\text{C}_2\text{H}_6\text{O}$, which is lost over sulphuric acid. The salt is intensely yellow, as is also the *ammonium* salt.

3-Bromo-4-hydroxybenzophenone, $\text{C}_{13}\text{H}_9\text{O}_2\text{Br}$, melts at 180 – 181° , forms colourless solutions in indifferent solvents, and yields a yellow *potassium* salt.

3:5-Dibromo-4-hydroxybenzophenone, $\text{C}_{13}\text{H}_5\text{OBr}_2$, melts at 151 – 152° , is colourless in all solvents, and forms colourless *potassium*, *barium*, *lead*, and *silver* salts.

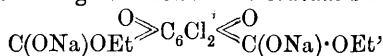
2:4-Dihydroxyacetophenone forms colourless solutions in cold alkali hydroxides, which become yellow by warming. The solid *lead*, *silver*, and *mercuric* salts are colourless. *2:4-Dihydroxypropiophenone* has been obtained in colourless crystals containing 1 mol., H_2O , and melting at 56° ; the anhydrous substance melts at 97.5° and forms colourless salts.

2-Hydroxy-5-methylbenzophenone is a merochromo-compound; the solution in light petroleum is colourless, but deposits yellow crystals. The acetyl and benzoyl derivatives, and the same compounds of all coloured aromatic hydroxyketones, are obtained colourless by treating the alkali salt suspended in ether or chloroform with the acid chloride.

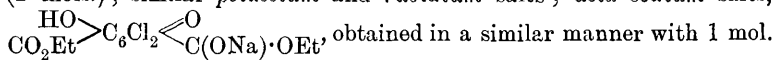
2:5-Dimethoxybenzophenone has been obtained colourless. *2:1-Acetylnaphthol* forms yellow solutions, except in light petroleum; the alkali and the barium salts are yellow, whilst the acetyl derivative

which melts at 107.5° , and the benzoyl derivative, which melts at 131° (compare Ullmann, Abstr., 1897, i, 482), are colourless when prepared as described above. The corresponding ethyl ketone is obtained conveniently by treating a solution of zinc chloride in propionic acid with α -naphthol at 160 — 170° ; its salts are yellow and the benzoyl derivative colourless. The brominated ketones form yellow needles and melt at 126 — 127° and at 98° respectively; their salts are yellow and the acetyl and benzoyl derivatives colourless.

The esters of the hydroxybenzoic acids and their derivatives do not form coloured salts. Selective absorption is first exhibited by the salts of acids containing two pairs of *o*-hydroxy and carbethoxy-groups. Ethyl dichloroquinoldicarboxylate forms colourless salts with tertiary amines ($\text{HO} > \text{C}_6\text{Cl}_2 < \text{OM}$), coloured compounds with secondary amines, and the following coloured salts: sodium salt,

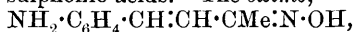


obtained from an alcoholic solution of the ester and sodium ethoxide (2 mols.); similar *potassium* and *rubidium* salts; *acid sodium* salts,



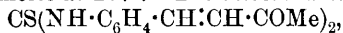
of sodium ethoxide; the yellow *ammonium* salt, $\text{C}_{12}\text{H}_{11}\text{O}_6\text{Cl}_2\cdot\text{NH}_4$, and the colourless salts with tertiary amines are obtained by the addition of ammonia or of the amine to an ethereal solution of the ester. The ester itself is colourless when solid or in cold alcoholic solution; when fused or in hot alcoholic solution, or in benzene or chloroform, it becomes greenish-yellow and is represented as a merochrome-compound. Similar colour relations are manifested by the salts of quinoldicarboxylic acid and its ethyl ester. C. S.

Methineammonium Dyes. III. HANS RUPE and O. SIEBEL (*Zeit. Farb. Ind.*, 1906, 5, 301—304. Compare Abstr., 1904, i, 107; 1905, i, 83).—*p*-Acetylaminobenzaldehyde, $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, prepared by warming *p*-aminobenzaldehyde with acetic anhydride, crystallises from toluene in yellow needles, melts at 141° , and condenses with acetone in presence of sodium hydroxide to form *acetyl-p-aminobenzylideneacetone*, $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{COMe}$; this crystallises from water in dull yellow needles, melts at 184° , and is hydrolysed by sulphuric acid in acetic acid solution, forming *p-aminobenzylideneacetone*, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{COMe}$, which crystallises from 50 per cent. methyl alcohol in yellow leaflets and melts at 81° . The base is best prepared by condensing commercial aminobenzaldehyde dissolved in 50 per cent. acetic acid with acetone. On adding dilute hydrochloric acid gradually to a suspension of the base in water, a deep red solution is first produced, which becomes colourless on adding more acid; this behaviour characterises the methineammonium bases. The red solution has strong tinctorial properties. Coloured azo-compounds are formed on coupling diazotised *p*-aminobenzylideneacetone with hydroxy- and amino-naphthalene sulphonics acids. The *oxime*,



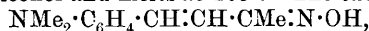
of the base, crystallises from alcohol and melts at 196° . The *benzoyl*

derivative, $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{COMe}$, crystallises from alcohol in yellow needles and melts at 207° . The *thiocarbamide*,

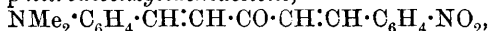


is sparingly soluble in all solvents and melts at 162° . The *hydrazone*, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CMe} : \text{N} \cdot \text{NH}_2$, forms scaly leaflets and melts at 92° .

p-Dimethylaminobenzylideneacetone, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{COMe}$, prepared from dimethylaminobenzaldehyde and acetone at the ordinary temperature, crystallises from alcohol in feebly yellow leaflets and melts at 132° ; the substance described under the same name by Sachs and Lewin (Abstr., 1903, i, 37) is probably a more complex condensation product. The *phenylhydrazone*, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CMe} : \text{N} \cdot \text{NHPh}$, crystallises from alcohol and melts at 165° . The *oxime*,



crystallises from alcohol in yellow leaflets and melts at 168° . *p*-Dimethylamino-*p*-nitrodibenzylideneacetone,



prepared by the condensation of dimethylaminobenzylideneacetone and *p*-nitrobenzaldehyde, crystallises from glacial acetic acid and melts at 215° ; the *hydrochloride*, $\text{C}_{19}\text{H}_{18}\text{O}_3\text{N}_2 \cdot \text{HCl}$, is blue, and is decomposed by water. *p*-Dimethylamino-*p*-aminodibenzylideneacetone, obtained by the reduction of the nitro-compound, crystallises from alcohol in intensely red leaflets and melts at 228° . W. A. D.

Dibenzylideneacetone and Triphenylmethane. I. FRITZ STRAUS and O. ECKER (*Ber.*, 1906, 39, 2977—3006).—*Distyryldichloromethane*, $\text{CCl}_2(\text{CH} : \text{CHPh})_2$, prepared by cautiously adding dry phosphorus pentachloride to a boiling solution of dibenzylideneacetone in benzene, forms clusters of silvery leaflets melting at 77° .

Distyryldichloromethane dichloride, $\text{CHPhCl} \cdot \text{CHCl} \cdot \text{CCl}_2 \cdot \text{CH} : \text{CHPh}$, formed by adding a saturated chloroform solution of chlorine to the ketochloride dissolved in the same solvent, crystallises from benzene and petroleum in radially-grouped needles melting at 133° . The corresponding *dibromide* crystallises in colourless prisms and melts and decomposes at 153° . *Distyryldichloromethane* when quite dry is not affected by hydrogen chloride, but when dissolved in cold concentrated sulphuric acid it gives a bluish-violet solution with reddish-violet fluorescence; the colour gradually changes to brownish-orange, especially on warming. Hydrogen chloride is evolved, and when the interaction is effected in carbon disulphide solution, the *sulphate*, $\text{C}_{17}\text{H}_{14}\text{Cl}_2 \cdot \text{SO}_4\text{H} \cdot \text{H}_2\text{SO}_4$, separates in violet crystals which are extremely sensitive to moisture. When treated with absolute ether, the violet crystals are decomposed, yielding dibenzylideneacetone and an oil containing chlorine. The ketochloride readily dissolved in liquid sulphur dioxide, and the solution had an appreciable electrical conductivity, although not so great as that of triphenylchloromethane in the same solvent.

Distyryldichloromethane combines with metallic chlorides, the *stannichloride*, $\text{C}_{17}\text{H}_{14}\text{Cl}_2 \cdot \text{SnCl}_4$, forms violet leaflets with a bronzy lustre, the *mercurichloride* separates in violet-brown needles. Methyl alcohol attacks the keto-chloride, ultimately eliminating both chlorine atoms in the form of hydrogen chloride, and yielding a red, crystalline sub-

stance which could not be purified; glacial acetic acid also removes one chlorine atom, the product being probably the carbinol acetate, $C(CH:CHPh)_2Cl \cdot OAc$.

Two *distyrylchlorocarbinol anhydrides*, $O \begin{array}{c} \diagup CCl(CH:CHPh)_2 \\ \diagdown CCl(CH:CHPh)_2 \end{array}$, are produced on shaking an ethereal solution of distyryldichloromethane with water, the total yield being about 40—50 per cent. of the keto-chloride. The mixture, when crystallised from benzene and light petroleum, yields large, hard, transparent prisms decomposing violently at 147° , and slender, soft, light needles decomposing at 167 — 169° . The substances differ in their behaviour towards warm glacial acetic acid; the prismatic substance furnishes a solid product, $C_{35}H_{20}OCl$, melting at 159 — 161° , whilst the acicular compound yields an oil.

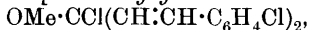
Di-p-chlorobenzylideneacetone, $CO(CH:CH \cdot C_6H_4Cl)_2$, prepared by condensing *p*-chlorobenzaldehyde and acetone in dilute alcoholic solution in the presence of sodium hydroxide, crystallises in well-defined yellow leaflets and melts at 193° .

Di-p-chlorostyryldichloromethane, $CCl_2(CH:CH \cdot C_6H_4Cl)_2$, obtained from the preceding compound by the action of phosphorus pentachloride in benzene solution, crystallises from ether in radial aggregates of thick, colourless prisms melting at 102 — 103° .

The *dibromide*, $C_6H_4Cl \cdot CHBr \cdot CHBr \cdot CCl_2 \cdot CH:CH \cdot C_6H_4Cl$, was obtained by treating the keto-chloride with bromine; it crystallises from benzene and petroleum in aggregates of colourless needles melting at 124 — 125° .

The *stannichloride*, $C_{17}H_{12}Cl_4 \cdot SnCl_4$, separates in fine, crystalline aggregates having a metallic lustre.

The *methyl ether of di-p-chlorostyrylchlorocarbinol*,



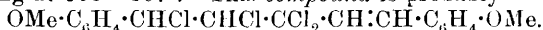
formed by adding a benzene solution of the keto-chloride to a methyl alcohol solution of sodium methoxide, separates from methyl alcohol in aggregates of white needles melting at 95 — 96.5° . It was not found possible to replace the second chlorine atom by methoxyl, neither could this halogen be removed by reducing agents.

Di-p-iodobenzylideneacetone, $CO(CH:CH \cdot C_6H_4I)_2$, was prepared by condensing *p*-iodobenzaldehyde and acetone in the presence of alkalis; when crystallised from pyridine, it separated in yellow leaflets melting at 254 — 255° . This ketone is sparingly soluble in the ordinary organic media.

Di-p-iodostyryldichloromethane, $CCl_2(CH:CH \cdot C_6H_4I)_2$, crystallises from petroleum in white, crystalline masses or from benzene in white needles melting at 146 — 147° .

Dianisylideneacetone and phosphorus pentachloride in benzene solution furnish the compound $CCl_2(CH:CH \cdot C_6H_4 \cdot OMe)_2$, $PCl_5 \cdot C_6H_6$, which separates in green leaflets. When the benzene solution of phosphorus pentachloride and dianisylideneacetone is heated for half an hour, the liquid no longer deposits the green compound on cooling; but on evaporation a grey, crystalline mass is obtained which, after purification, crystallises from carbon disulphide in colourless prisms melting and

decomposing at $106-107^{\circ}$. This compound is probably



Benzophenone dichloride, when treated with methyl alcohol, furnishes dimethoxydiphenylmethane.

The characteristic behaviour of many of these chloro-derivatives with sulphuric acid is described in detail. G. T. M.

Ketenes. III. Diphenyleneketene. HERMANN STAUDINGER (*Ber.*, 1906, **39**, 3062—3067. Compare *Abstr.*, 1905, i, 444; this

vol., i, 234).—*Chlorodiphenyleneacetyl chloride*, $\text{C}_6\text{H}_4 > \text{C}_6\text{H}_4 > \text{CCl} \cdot \text{COCl}$, is formed in 50 per cent. yield when phosphorus pentachloride reacts with diphenyleneglycollic acid in cold chloroform; it melts at $111.5-112.5^{\circ}$, and reacts with water to regenerate the acid, with alcohol to form ethyl chlorodiphenyleneacetate, which melts at $46-47^{\circ}$, and with aniline to form the *anilide*, $\text{C}_{20}\text{H}_{14}\text{ONCl}$, which melts at 177° .

Diphenyleneketene, $\text{C}_6\text{H}_4 > \text{C} : \text{C} < \text{C}_6\text{H}_4$, obtained by the action of zinc on the preceding chloride in ether in the absence of air and moisture, melts at $90-90.5^{\circ}$ to a red liquid, decomposes at 150° , and gives an indigo blue coloration with concentrated sulphuric acid. With excess of water it yields diphenyleneacetic acid, whilst the addition of the requisite amount of water to the ketene dissolved in benzene or light petroleum precipitates the *anhydride*, $\text{C}_{28}\text{H}_{18}\text{O}_3$, which melts at $164-165^{\circ}$.

Ethyl diphenyleneacetate, prepared from the ketene and ethyl alcohol, or by esterifying the acid, melts at $43-45^{\circ}$ and boils at $209-210^{\circ}$ under 17 mm. pressure. The *anilide*, $\text{C}_{20}\text{H}_{15}\text{ON}$, separates from xylene in slender needles and melts at 255° ; the *phenylhydrazide* melts at $234-235^{\circ}$.

From solutions of the ketene in light petroleum, tertiary bases such as quinoline, quinaldine, pyridine, or triethylamine precipitate additive compounds which are decomposed by water; the quinoline compound, $2\text{C}_{14}\text{H}_9\text{O} \cdot \text{C}_9\text{NH}_7$, is a white, crystalline powder which darkens at 140° and melts and decomposes at $154-155^{\circ}$. These additive compounds are stable to oxygen, but behave like the ketenes to water, alcohol, aniline, phenylhydrazine, and the Schiff bases. The quinoline compound reacts with water to form a mixture of diphenyleneacetic acid and *quinoline diphenyleneacetate*, $\text{C}_{14}\text{H}_{10}\text{O}_2 \cdot \text{C}_9\text{NH}_7$; the latter melts at $109-110^{\circ}$.

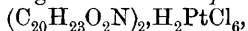
Bisdiphenyleneallene, $\text{C}_6\text{H}_4 > \text{C} : \text{C} < \text{C}_6\text{H}_4$, forms orange-yellow needles and is obtained by heating the quinoline additive compound with quinoline diphenyleneacetate.

The zinc chloride precipitated in the preparation of diphenyleneketene contains a considerable quantity of the ketene. When the precipitate is oxidised by atmospheric oxygen, fluorenone and a substance, $\text{C}_{28}\text{H}_{16}\text{O}_3$, which melts at $269-270^{\circ}$ are obtained; the latter is regarded as a tetra-

substituted derivative of tetrionic acid, $\text{C}_6\text{H}_4 > \text{C} < \begin{array}{c} \text{CO} \cdot \text{O} \\ \text{CO} \end{array} < \text{C} < \text{C}_6\text{H}_4$.
C. S.

Derivatives of Benzoylacetone. GIOVANNI ISSOGLIO (*Atti R. Accad. Torino*, 1906, 41, 946—960).—When benzoylacetone is treated with acetaldehyde in presence of concentrated ammonia solution, it reacts as if it possessed the enolic structure of β -hydroxy- α -benzoylpropylene, $\text{OH}\cdot\text{CMe}\cdot\text{CHBz}$, the following products being obtained.

(1) *Dibenzoyldiisopropylamine*, $\text{NH}(\text{CHMe}\cdot\text{CH}_2\text{Bz})_2$, crystallises from benzene in shining, rhombic plates melting at 127° , dissolves in alcohol or chloroform, and to a slight extent in ether, and has the normal molecular weight in freezing benzene. The *platinichloride*,



forms an amorphous precipitate melting at 198° , and the *picrate*, $\text{C}_{20}\text{H}_{23}\text{O}_2\text{N}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OH}$, crystallises in microscopic, fern-like aggregates of yellow needles melting and decomposing at 192° .

(2) β -*Ethylidenedibenzoylacetone*, $\text{CHAcBz}\cdot\text{CHMe}\cdot\text{CBz}\cdot\text{CMe}\cdot\text{OH}$, crystallises from 60 per cent. alcohol in white needles with a silvery lustre, melts at 134° , and dissolves readily in alcohol, acetone, or chloroform, and less so in benzene.

(3) 3:5-*Dibenzoyl-2:4:6-trimethyl-1:4-dihydropyridine* (3:5-*dibenzoyl-1:4-dihydrocollidine*), $\text{CHMe}\langle\begin{smallmatrix} \text{CBz}\cdot\text{CMe} \\ \text{CBz}\cdot\text{CMe} \end{smallmatrix}\rangle\text{NH}$, crystallises from alcohol in slender, straw-yellow needles, begins to turn brown at 200° , and melts at 238 — 239° , and is slightly soluble in acetone, chloroform, or benzene.

T. H. P.

The Employment of Vanadium Salts in the Electrolytic Oxidation or Reduction of Organic Compounds. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 172654).—Vanadium salts are very suitable depolarisers either at the anode or cathode, and the attack of the oxygen or hydrogen on the organic substance is greatly accelerated.

Finely-pulverised anthracene (4 kilograms) is introduced into a leaden anode cell containing 100 litres of 20 per cent. sulphuric acid with 3 per cent. of vanadic acid. The current density is 300 amperes per square metre with 1.8 volts. After filtering off the anthraquinone, which is rapidly produced in good yield, the electrolytic solution is ready for a further quantity of anthracene.

By the aid of vanadium salts, aniline may be oxidised to benzoquinone, and the latter then reduced to quinol. Azobenzene and azoxybenzene suspended in 20 per cent. sulphuric acid containing two parts of vanadium trioxide are reduced to benzidine in the cathode cell.

G. T. M.

Preparation of Derivatives of the Reduction Products of Anthraquinone. BADISCHE ANILIN- UND SODA-FABRIK (D.R.-P. 172930).—The reduction products of anthraquinone, anthranol, hydroxyanthranol and their homologues and sulphonic acids condense with aldehydes to yield substances which are insoluble in alkalis.

Anthranol, when condensed with benzaldehyde in concentrated sulphuric acid at 30 — 35° , yields a substance which, when crystallised from alcohol, separates in needles melting at 112 — 114° ; this compound is indifferent towards dilute acids or alkalis, but develops a

magenta coloration with concentrated sulphuric acid. A similar substance can be obtained with hydroxyanthranol.

Anthranol also condenses with para-acetaldehyde: the product is an olive-yellow powder, insoluble in dilute acids or alkalis, but dissolving in concentrated sulphuric acid to a reddish-brown, fluorescent solution.

G. T. M.

Preparation of the Urethanes of Polynitroaminoanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 171588).—It is not possible to introduce into the aminoanthraquinones and their acetyl derivatives more than one nitro-group, and only two of these groups can be introduced into the diaminoanthraquinones and their diacetyl compounds. The urethanes of these amino- and diaminoanthraquinones, on the other hand, can be nitrated readily to furnish polynitro-derivatives which on hydrolysis yield polynitroaminoanthraquinones of great technical importance. The hydrolysis is carried out by heating the nitrated urethane in concentrated sulphuric acid at 80° until the evolution of carbon dioxide ceases. In this way, the following compounds were prepared: 2:4-dinitro-1-aminoanthraquinone, 1:3-dinitro-2-aminoanthraquinone, 2:4:6:8-tetranitro-1:5-diaminoanthraquinone, and 2:4:5:7-tetranitro-1:8-diaminoanthraquinone.

These compounds develop characteristic colorations when dissolved in pyridine, concentrated and fuming sulphuric acid, or in a mixture of sulphuric and boric acids.

G. T. M.

Methylation of Hydroxyanthraquinones. CARL GRAEBE (*Annalen*, 1906, 349, 201—207. Compare Abstr., 1905, i, 219).—An introduction to the two papers following.

A hydroxy-group in position 1 in anthraquinone is either not methylated or is only very slightly methylated by methyl iodide. A more complete methylation is accomplished by acting on the deoxy-compound, which is afterwards readily oxidised to the anthraquinone ether.

The action of fuming sulphuric acid on alizarin, followed by heating the product with concentrated sulphuric acid, leads to the formation of quinalizarin, hydroxyanthrarufin (which is isolated from the residue by means of boiling toluene, crystallises in red needles, melts at $270-273^{\circ}$, and gives a violet coloration with sodium hydroxide or concentrated sulphuric acid) and 1:2:5-trihydroxyanthraquinone-sulphonic acid, $C_{14}H_9O_8S$, which is obtained also on prolonged heating of quinalizarin with sulphuric acid; it is obtained as a reddish-yellow precipitate, gives with alkali hydroxides a violet, with acetates a yellowish-red coloration, and yields hydroxyanthrarufin when heated alone or with hydrochloric acid at $180-200^{\circ}$.

G. Y.

Ethers of Alizarin, Flavopurpurin, Hydroxyanthrarufin, and Hydroxychrysazin. CARL GRAEBE and CARLOS THODE (*Annalen*, 1906, 349, 207—222. Compare preceding abstract, Abstr., 1905, i, 219; Farbenfabriken vorm. Fr. Bayer & Co., Abstr., 1905, i, 362, 532).—Deoxyalizarin dimethyl ether (1:2-dimethoxyanthrone),

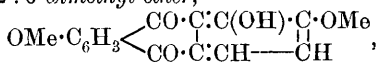
$C_6H_4 \begin{smallmatrix} <CH_2> \\ <CO- \end{smallmatrix} C_6H_2(OMe)_2$, prepared by the action of methyl sulphate on deoxyalizarin in 10 per cent. aqueous sodium hydroxide, crystallises in yellow needles, melts at 150° , forms a yellow solution in alcohol or benzene, showing a blue fluorescence when very dilute, and gives a yellow to yellowish-brown coloration with concentrated sulphuric acid. It is insoluble in aqueous sodium hydroxide, is only slowly attacked by boiling alkali hydroxides, remains unchanged when heated with 78 per cent. sulphuric acid at 100° , and does not form an acetyl derivative or an oxime. The *diethyl ether*, $C_{18}H_{18}O_3$, crystallises in yellow needles, melts at 128° , gives a yellow to yellowish-brown coloration with concentrated sulphuric acid, and on oxidation yields alizarin diethyl ether.

Alizarin 2-monomethyl ether is formed in small quantity, together with the dimethyl ether, by the action of methyl sulphate on alizarin; it is separated from the dimethyl ether by shaking the benzene solution with aqueous sodium hydroxide. It is obtained also by hydrolysis of the dimethyl ether with sulphuric acid on the water-bath.

Reduction of alizarin dimethyl ether by means of zinc dust and ammonia leads to the formation of deoxyalizarin dimethyl ether, together with an impure *ether*, which is formed also by reduction of deoxyalizarin dimethyl ether, melts at a lower temperature, and on oxidation with chromic acid and glacial acetic acid yields alizarin dimethyl ether.

Alizarin diethyl ether, $C_{18}H_{16}O_4$, prepared in a 2 per cent. yield, together with a 5 per cent. yield of the 2-monoethyl ether, by the action of ethyl sulphate on alizarin in aqueous sodium hydroxide solution on the water-bath, crystallises in yellow needles, melts at 162° , and yields the 2-monoethyl ether when heated with 78–80 per cent. sulphuric acid on the water-bath. The descriptions of the diethyl ether given by previous authors are erroneous.

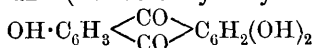
Flavopurpurin-2 : 6-dimethyl ether,



prepared by heating the sodium derivative of flavopurpurin with methyl sulphate at 160° , or by heating the trimethyl ether with sulphuric acid at 100° , crystallises from a mixture of chloroform and carbon disulphide in yellow needles, melts at 239° , forms yellow solutions, is extracted from its solution in benzene or chloroform when shaken with aqueous sodium hydroxide, and forms a red *sodium* derivative and an *acetyl* derivative, $C_{18}H_{14}O_6$, which crystallises from glacial acetic acid and melts at 210° .

Deoxyflavopurpurin forms a yellow, crystalline precipitate and melts at 258° ; when heated with methyl sulphate and 10 per cent. sodium hydroxide in an atmosphere of coal gas and oxidised with sodium dichromate and glacial acetic acid, it forms flavopurpurin trimethyl ether, melting at 225 – 226° , in a 30 per cent. yield.

Hydroxyanthrarufin (1 : 2 : 5-trihydroxyanthraquinone),



(compare Graebe, Abstr., 1891, 463), prepared by heating anthrarufin

with sodium nitrate and aqueous sodium hydroxide under pressure at 180—185°, crystallises from glacial acetic acid in yellow or brownish-red needles, melts at 273—274°, forms a violet solution in aqueous alkali hydroxides, gives with concentrated sulphuric acid a violet coloration becoming blue on addition of boric acid, and shows a spectrum with three dark bands of 645—625, 590—570, and 545—530 μ respectively; it dyes mordanted cotton, colours resembling those obtained with alizarin, but more bluish-red when the mordant is alumina. The *triacetate*, $C_{20}H_{14}O_8$, crystallises from alcohol in yellow needles and melts at 229°. The *2-methyl ether* of hydroxyanthrarufin, $C_{15}H_{10}O_5$, formed by the action of methyl sulphate and sodium hydroxide on hydroxyanthrarufin, is obtained as a yellow precipitate, melts after recrystallisation from alcohol at 202°, and is not a dye. 1 : 2 : 5-*Trihydroxyanthrone* (*deoxyhydroxyanthrarufin*), $C_{14}H_{10}O_4$, prepared by reduction of hydroxyanthrarufin with zinc dust in dilute ammoniacal solution, melts at 258°; when treated with methyl sulphate and $4\frac{1}{2}$ mols. of sodium hydroxide, it yields a *monoethyl ether*, $C_{15}H_{12}O_4$, which crystallises from alcohol and melts at 140°.

Hydroxychrysazin (1 : 2 : 8-trihydroxyanthraquinone) crystallises in orange needles, melt at 230° (corr.), forms solutions similar to those of anthrapurpurin, dyes cotton-wool mordanted with alumina brownish-red, or with iron a violet-grey, and gives with sulphuric acid a red coloration becoming violet on addition of boric acid. The *triacetate* melts at 218—219° (compare Liebermann and Giesel, this Journal, 1876, i, 711). On reduction with zinc dust and ammonia on the water-bath, treatment with methyl sulphate and sodium hydroxide, and oxidation with sodium dichromate in boiling glacial acetic acid solution, hydroxychrysazin forms the *trimethyl ether*, $C_{17}H_{14}O_5$, which crystallises from methyl alcohol, melts at 157°, and is soluble in benzene or chloroform, but is insoluble in aqueous sodium hydroxide. When heated with sulphuric acid on the water-bath, it is hydrolysed principally to the *dimethyl ether*, $C_{16}H_{12}O_5$, forming yellow crystals and melting at 193°, together with small quantities of the *2-monomethyl ether*, $C_{15}H_{10}O_5$; this is prepared by the action of methyl sulphate on hydroxychrysazin in alkaline solution, crystallises in orange-yellow needles, melts at 220°, and is soluble in aqueous sodium hydroxide, but not in the carbonate.

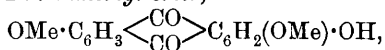
G. Y.

Methyl Ethers of 2- and 1-Hydroxyanthraquinones, Anthrapurpurin, Purpurin, and Purpuroxanthin. CARL GRAEBE and HEINRICH BERNHARD (*Annalen*, 1906, 349, 222—231. Compare preceding abstracts).—2-Methoxyanthraquinone, formed by the action of methyl sulphate on 2-hydroxyanthraquinone in alkaline solution, is identical with Kautler's product from 2-nitroanthraquinone (*Abstr.*, 1904, i, 256).

1-Methoxyanthraquinone is formed only in small quantities by the action of methyl sulphate on erythroxyanthraquinone, but in better yields by the action of methyl sulphate at 100°, or of potassium methyl sulphate at 200°, on the sodium derivative of erythroxyanthraquinone, or by successive reduction of the anthraquinone with zinc dust and glacial acetic acid, methylation, and oxidation; it crystallises from alcohol, melts at 169.5°, and is more stable than alizarin dimethyl

ether towards sulphuric acid, being hydrolysed to 1-hydroxyanthraquinone only very slowly. 1-Methoxyanthrone, $C_{15}H_{10}O_2$, melts at 105° .

Anthrapurpurin melts at 369° , the triacetate, $C_{20}H_{14}O_8$, melts at $223-224^\circ$. The 2:7-dimethyl ether,



prepared by the action of an excess of methyl sulphate and sodium hydroxide on anthrapurpurin, or by the action of 78 per cent. sulphuric acid on anthrapurpurin trimethyl ether on the water-bath, crystallises from benzene, melts at 241° , and forms a red sodium derivative.

The trimethyl ether of anthrapurpurin, $C_{17}H_{14}O_5$, prepared by methylation and oxidation of deoxyanthrapurpurin, crystallises from alcohol in yellow needles, melts at 201° , and is readily soluble in benzene, chloroform, or hot alcohol.

The action of an excess of sodium hydroxide and methyl sulphate on purpurin leads to the formation of the 2-monomethyl ether. The 3-methyl ether of purpuroxanthin, $C_{15}H_{10}O_4$, formed by the action of methyl sulphate and sodium hydroxide on purpuroxanthin, crystallises from benzene and melts at 193° ; the benzene mother liquors contain a dimethyl ether crystallising in yellow needles and melting at $150-153^\circ$ (compare Boeck, Abstr., 1905, i, 531). G. Y.

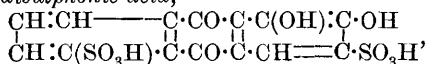
Conversion of Aromatic Ketones into the Corresponding Imides. MAURICE PRUD'HOMME (*Bull. Soc. chim.*, 1906, [iii], 35, 666-668. Compare this vol., i, 193).—Hydroxyanthraquinones may be readily converted into the corresponding imides by heating them in glycerol with a normal ammonium salt of an organic acid or with ammonium carbonate. Under similar conditions, tetramethyldiaminobenzophenone furnishes auramine. "Alizarin yellows A and C," when treated in this way, yield products giving yellow and olive tints with the usual mordants, which are different from those given by the original dyes.

When alizarin is fused with ammonium thiocyanate in place of ammonium carbonate, or sulphur is added to a mixture of alizarin, glycerol, and the organic ammonium salt used to produce alizarinimide in the above reaction, the sulphur appears to enter into combination and to modify the tinctorial properties of the alizarinimide formed.

T. A. H.

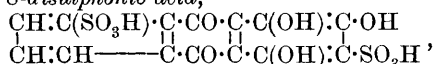
Preparation of Hydroxyanthraquinonesulphonic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 172688. Compare Abstr., 1905, i, 146).—The treatment of anthraquinone- α -sulphonic acid with fuming sulphuric acid containing a high percentage of sulphur trioxide leads to the introduction of hydroxyl groups into the anthracene nucleus. It is now found that the same result is obtained when acid containing less than 45 per cent. of sulphur trioxide is employed either with or without boric acid. Small quantities of mercury salts are found in many cases to accelerate the oxidation.

Alizarin-3:5-disulphonic acid,



is produced by heating at 130—135° a mixture of potassium anthraquinone- α -sulphonate, boric acid, and fuming sulphuric acid containing 40 per cent. of sulphur trioxide. The *acid potassium* salt of alizarin-3:5-disulphonic acid crystallises on pouring the acid fusion into ice-cold water, whilst the quinizarin- α -sulphonic acid also produced in this reaction remains in solution and is precipitated with sodium chloride. Alizarin-3:5-disulphonic acid, when heated at 180° with 70 per cent. sulphuric acid, yields alizarin-5-sulphonic acid.

Purpurin-3:8-disulphonic acid,



is produced by heating potassium anthraquinone-1:5-disulphonate with boric acid and fuming sulphuric acid (40 per cent. SO_3), under 6 to 7 atmospheres pressure. When poured into water, the fusion yields the *acid potassium* salt of this acid, which, when crystallised from dilute hydrochloric acid, separates in yellowish-red leaflets or prisms having a bronzy lustre. When heated at 180° with 70 per cent. sulphuric acid, the foregoing disulphonic acid furnishes purpurin- α -sulphonic acid; if a mercury salt is added, purpurin itself is formed.

Other di- and tri-hydroxyanthraquinonesulphonic acids can be prepared similarly by the foregoing process, and the properties of some of these products are tabulated in the patent. G. T. M.

Preparation of Chlorinated Quinazarins. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 172105).—Chlorinated quinazarins may be prepared by condensing quinol with those chlorophthalic acids which contain not more than one halogen atom in an ortho-position with respect to the carboxyl groups.

Quinol and 4:5-dichlorophthalic anhydride are heated at 155—160° for four hours in concentrated sulphuric acid, either alone or with the addition of boric acid; the product is poured into water, dissolved in an aqueous alkali hydroxide and reprecipitated by dilute acid. When crystallised from glacial acetic acid, it separates in brownish-red leaflets melting at 255°. Its solutions are bluer than those of quinazarin itself; that in concentrated sulphuric acid assumes a yellow fluorescence on the addition of boric acid.

5-Chloroquinazarin, obtained from quinol and 3-chlorophthalic acid, crystallises from glacial acetic acid in brownish-red needles melting at 240°. G. T. M.

Bluish-green Colouring Matters of the Anthracene Series. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 172575).—When dinitroanthrarufindisulphonic acid is reduced with alkali sulphides in alkaline solutions, the reaction leads readily to the formation of diaminoanthrarufindisulphonic acid. If, however, the nitrosulphonic acid is reduced with sulphide in neutral solution, then beside the diamino-derivative a new product is formed, and this is obtained exclusively when alkali hydrosulphide is used instead of a sulphide. Although the exact nature of this new substance has not yet been ascertained, it is probably a partial reduction product such as a hydroxylamino- or a nitroamino-derivative, but it has not yet been

found possible to complete its reduction to diaminoanthrarufindisulphonic acid (Alizarinsaphirol β). The new product differs from the diamino-derivative in several of its colour reactions and also in tinctorial properties. These characteristic differences are arranged in the patent in tabular form.

G. T. M.

Preparation of *p*-Nitro-derivatives of the α -Hydroxyanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 170728).—The nitration of the α -hydroxyanthraquinones themselves leads to the production of a complex mixture of isomerides of which only the *p*-nitro-derivatives are of technical importance. It is therefore preferable to nitrate the aryl ethers of the α -hydroxyanthraquinones, as on hydrolysis the nitro-compounds thus obtained yield exclusively the required *p*-nitro-derivatives.

The diphenyl ether of anthrarufin on nitration yields the hexanitro-compound, $\text{CH:C}[\text{O}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2]\cdot\text{C}\cdot\text{CO}\cdot\text{C}\cdot\text{C}(\text{NO}_2)=\text{CH}$
 $\text{CH:C}(\text{NO}_2)=\text{C}\cdot\text{CO}\cdot\text{C}\cdot\text{C}[\text{O}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2]\cdot\text{CH}$, which on alkaline hydrolysis gives rise to 2:4-dinitrophenol and *p*-dinitroanthrarufin.

The diphenyl ester of chrysazin gives a similar hexanitro-compound which on hydrolysis furnishes 2:4-dinitrophenol and *p*-dinitrochrysazin.

G. T. M.

Preparation of Dichlorochrysazin. R. WEDEKIND & Co. (D.R.-P. 172300).—Chrysazin is not affected by chlorinating agents at 100°, but when 10 parts of this substance are suspended in 1000 parts of concentrated sulphuric acid diluted with their own weight of water and heated at 125°, while a solution of 20 parts of potassium chlorate and 80 parts of sodium chloride also dissolved in the same quantity of water is slowly added, chlorination takes place readily, and *pp*-dichlorochrysazin separates in well-defined orange-coloured crystals.

G. T. M.

Preparation of 1:2:2':1'-Anthrazine. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 172684).—1:2:2':1'-Anthrazine, which was formerly obtained with great difficulty by the reduction of indanthrene, a substance formed by fusing β -aminoanthraquinone with alkali hydroxides, is now prepared by heating β -anthramine with a mixture of sodium and potassium hydroxides at 220–230° in the absence of air. The anthrazine, which forms a dark layer on the alkali, is easily separated and obtained pure by recrystallisation from nitrobenzene.

G. T. M.

Thioborneol. WALTHER BORSCHKE and W. LANGE (*Ber.*, 1906, 39, 3268).—Thioborneol, described recently by the authors (this vol., i, 679), had been obtained previously by Wuyts (*Abstr.*, 1903, i, 428).

C. S.

Artificial Production of Camphor from Turpentine Oil. OTTO SCHMIDT (*Chem. Centr.*, 1906, ii, 722; from *Chem. Ind.*, 29, 241–244).—The yield of camphor obtained by initially treating the

crude oil with hydrochloric acid is very nearly the same (25 per cent.) as that obtained by the use of oxalic or salicylic acid. The conversion of pinene into bornyl and isobornyl esters is readily effected by means of *o*-chlorobenzoic acid, which is more stable than salicylic acid and, therefore, to be preferred to the latter. H. M. D.

The Isolation of ψ -Ionone Hydrate and an Isomeride. P. COULIN (D.R.-P. 172653).—When moderately concentrated acids act on ψ -ionone even at the ordinary temperature, there is produced, together with ionone, hydrocarbons and tarry matters, a certain amount of substances, the boiling points of which are higher than those of ionone, ψ -ionone, or the hydrocarbons. It is now shown that this mixture contains ψ -ionone hydrate and an isomeride, $C_{13}H_{22}O_2$, and that these two compounds can be separated by means of alkali sulphites, in solutions of which the ψ -ionone hydrate readily dissolves, whilst its isomeride is insoluble. This isomeric substance is a viscid oil boiling at 166.8° to 169.8° under 10.5 mm. pressure and having a refractive index 1.50647 at 21° ; it slowly solidifies to a crystalline mass melting at 80° ; its *semicarbazone*, which is formed quantitatively, crystallises readily and melts and decomposes at 228° .

The ψ -ionone hydrate is isolated from the sodium sulphite solution by making this strongly alkaline and extracting with ether or benzene; it boils at 180 — 182° under 12 mm. pressure, and has a sp. gr. 0.954 at 15° and n_D 1.53322 at 20° . G. T. M.

Oils from Conifers. R. E. HANSON and E. N. BABCOCK (*J. Amer. Chem. Soc.*, 1906, 28, 1198—1201).—The following volatile oils, with the exception of the first two and the last, are now described for the first time.

The leaves of the black spruce (*Picea Mariana*) yield 0.57 per cent. of an oil which has a sp. gr. 0.9274 at 19° .

Samples of oil distilled from the leaves and twigs of the hemlock (*Tsuga canadensis*) were obtained in yields of 0.4 and 0.46 per cent., and had a sp. gr. 0.9238 and 0.9273 respectively at 15° .

The leaves of the cat spruce (*Picea canadensis*) yield 0.103 per cent. of an oil which has a sp. gr. 0.9216 at 15° , and contains 25.7 per cent. of esters (calculated as bornyl acetate).

The leaves of the red spruce (*Picea rubens*) furnish 0.204 per cent. of an oil which has an agreeable odour and a sp. gr. 0.9539 at 16° , and contains 7.76 per cent. of borneol and 66.2 per cent. of bornyl acetate.

The leaves and twigs of the American larch (*Larix americana*) yield 0.149 per cent. of an oil which has a sp. gr. 0.8816 at 15° and consists chiefly of pinene together with 15.1 per cent. of esters (calculated as bornyl acetate).

The cones of *Picea rubens* yield 0.38 per cent. of a golden-yellow oil which has a sp. gr. 0.8600 at 15° .

The cones of *Picea canadensis* yield 0.25 per cent. of a yellow oil which has a limonene-like odour and a sp. gr. 0.899 at 15° .

The leaves and twigs of the pitch pine (*Pinus rigida*) furnish a

very small quantity (0.2 c.c. from 12 kilograms) of a yellow oil which has an extremely pungent odour.

The red pine (*Pinus resinosa*) yields about 0.001 per cent. of a pungent, brown oil.

The leaves and twigs of *Juniperus communis* furnish 0.15—0.18 per cent. of a light yellow oil which has a sp. gr. 0.8531 at 20°.

The oil distilled from the leaves of *Juniperus virginiana* has a sp. gr. 0.900 at 16°. E. G.

Action of Phenols and Naphthalene on Copals. CH. COFFIGNIER (*Bull. Soc. chim.*, 1906, [iii], 35, 762—767).—Madagascar copal and the products obtained from it (1) by "running" by the usual pyrogenetic process and (2) by heating it at 260—290° in closed vessels with naphthalene by Terrisse's process (*Brev. francais*, 334, 300, Oct. 1904) have been compared. The product obtained by "running" copal in the usual way is less soluble in alcohols, acetone, and amyl acetate, and more soluble in ether, turpentine oil, benzene, and chloroform than the crude copal. That prepared by Terrisse's process, when compared with the crude copal, is slightly less soluble in methyl alcohol, more soluble in chloroform, ether, turpentine oil, and benzene, whilst the solubility in ethyl alcohol and acetone remains practically unchanged.

Both products show a higher specific gravity, a lower melting point, a lower acid number, and a lower Kottstorfer number than the raw copal. There is no loss of weight when Terrisse's process is used and the product is lighter in colour than that obtained by the usual method. T. A. H.

American Colophony. PAUL LEVY (*Ber.*, 1906, 39, 3043—3046).—The abietic acid, $C_{19}H_{29} \cdot CO_2H$, obtained by the author from American colophony, although identical crystallographically with the acid prepared by other workers, differs from this in melting point and in its capacity for crystallising. American colophony, on distillation under reduced pressure, yields an oily hydrocarbon, $C_{19}H_{30}$, which, after purification, boils at 210—211° under 26.5 mm. pressure, and has a sp. gr. 0.977 at 20°. This substance is readily soluble in ether and benzene, and is not very miscible with alcohol.

The foregoing hydrocarbon is undoubtedly identical with Deville, and Bischoff and Nastvogel's "colophene," and with Easterfield and Bagley's "abietene" (compare *Trans.*, 1904, 85, 1238).

Abietic acid, when treated with phosphorus pentachloride or thionyl chloride, furnishes an acid chloride, which, however, was not isolated in a state of purity, since it decomposes on distillation under reduced pressure. By repeated fractionation, an oily fluorescent hydrocarbon was obtained from the products of this decomposition, which boiled at 200—202° under 17 mm. pressure. To this substance, which is formed in accordance with the following equation, $C_{19}H_{29} \cdot COCl = C_{19}H_{28} + CO + HCl$, the author gives the name abietin. Towards organic solvents it behaves like abietene, and appears to correspond with the substance obtained by Kraemer and Spilker by the dry distillation of colophony (compare *Abstr.*, 1900, i, 150). G. T. M.

The Identity of Thudichum's Phrenosin and Thierfelder's Cerebron. WILLIAM J. GIES (*J. Biol. Chem.*, 1906, 2, 159—182).—Thierfelder does not admit the identity of these two substances, although he admits on precisely the same grounds the identity of his cerebron with Gamgee's pseudo-cerebrin. The present paper is partly an historical literary retrospect into the subject, and is largely polemical. The identity of the two materials is maintained, as Gies and Posner originally stated. W. D. H.

Fern Secretions. I. Glandular Secretions of *Gymnogramme chrysophylla* and *G. calomelanos*. WILHELM ZOPF (*Chem. Centr.*, 1906, ii, 690—691; from *Ber. Deut. bot. Ges.*, 24, 264—272).—From the extract obtained by momentary immersion of the fronds of *Gymnogramme chrysophylla* in ether, two substances have been isolated: a colourless, neutral wax, which melts at 63—64°, and *gynogrammen*, $C_{18}H_{18}O_5$, which crystallises in red, plate-like prisms, probably monoclinic, melts at 159°, and has an aromatic odour. It is insoluble in water, but dissolves readily in cold acetone and alcohol. It is decomposed by alkali solutions, gives a red colour with ferric chloride, and dissolves in concentrated sulphuric acid with an intense golden-yellow colour. On boiling with ethyl alcohol, it yields *gymnogrammidin*, which forms colourless needles melting at 114—115°.

From *Gymnogramme calomelanos*, a colourless substance, *calomelanen*, $C_{20}H_{22}O_8$, has been obtained; it has a camphoraceous odour, crystallises in small needles, melts at 141—142°, and dissolves readily in ethyl ether and ethyl alcohol. It gives a red colour with ferric chloride, and dissolves in concentrated sulphuric acid with a yellow colour. Boiling water decomposes it, and yields a volatile substance, which also has an odour resembling that of camphor. H. M. D.

Brazilin and Hæmatoxylin. JOSEF HERZIG and JACQUES POLLAK (*Monatsh.*, 1906, 27, 743—771. Compare Abstr., 1903, i, 270, 713; 1904, i, 81, 333; 1905, i, 605; this vol., i, 198).—The authors compare their structural formula for brazilin with that suggested by Pfeiffer (*Chem. Zeitschr.*, 1904, 3, 390, 420) which closely resembles it.

When heated with acetic anhydride, sodium acetate, and zinc dust, the phenylhydrazine derivative of tetramethylhæmatoxylone forms a reduced *acetyl* derivative, $C_{24}H_{16}O_2N_2(OMe)_4$, which crystallises in white needles and melts at 188—192°.

[With ROBERT FISCHER.]—The isomeride obtained from tetramethylhæmatoxylone is readily soluble in aqueous alkali hydroxides, and can be titrated sharply with phenolphthalein as indicator. When boiled with alcoholic potassium hydroxide or with alcoholic hydrogen chloride, it forms a *methyl ether*, $C_{16}H_7O_2(OMe)_5$, which crystallises from alcohol, melts at 99—102°, and when boiled with aqueous-alcoholic potassium hydroxide is hydrolysed, forming the isomeride of tetramethylhæmatoxylone melting at 169—171°. The methyl ether remains unchanged when boiled with acetic anhydride and sodium acetate; in alcoholic solution, it forms with concentrated sulphuric acid a red ring which disappears on shaking, but if sufficient acid is added the whole

mixture becomes red, and the methyl ether is converted into β -dehydrotetramethylhæmatoxylin. The isomeride melting at $169-171^{\circ}$ does not react with hydroxylamine or with phenylhydrazine, and is not reduced by zinc dust in boiling glacial acetic acid solution.

[With WOLFGANG KLUGER.]—Acetyltrimethylbrazilin has $[\alpha]_D + 128^{\circ}14'$ at 20° or $+125^{\circ}54'50''$ at 22° . Acetyltetramethylhæmatoxylin has $[\alpha]_D + 151^{\circ}28'32''$ to $+152^{\circ}11'54''$ at 20° . As tetra-acetyl-brazilin prepared by acetylation of brazilin has $[\alpha]_D + 76^{\circ}24'31''$, and that prepared by simultaneous reduction and acetylation of brazilein has $[\alpha]_D + 75^{\circ}26'30''$, von Kostanecki and Feuerstein's formulæ for brazilin, which has one, and for brazilein, which has no asymmetric carbon atom, are probably incorrect. Almost all reactions of brazilin or its alkyl derivatives lead directly to the formation of inactive substances.

The triacetyl compound, $C_{16}H_9O(OAc)_3$ (Abstr., 1902, i, 482), and tetra-acetyl compound, $C_{16}H_8(OAc)_4$ (Abstr., 1901, i, 478), obtained by simultaneous reduction and acetylation of brazilin, have $[\alpha]_D - 30'14''$ and $+3^{\circ}22'46''$ respectively.

Two preparations of trimethylbrazilone obtained by oxidation of trimethylbrazilin with chromic acid in acetic acid solution have $[\alpha]_D + 1^{\circ}34'4''$ and $-1^{\circ}10'33''$ respectively. Brazilinic acid has $[\alpha]_D + 13'53''$.

The formation of γ -tetramethyldehydrobrazilin by heating trimethylbrazilone with methyl iodide and potassium hydroxide on the water-bath is confirmed (compare Abstr., 1902, i, 482; 1904, i, 908).

[With ADOLF MAYRHOFER.]—The action of diacetylorthonitric acid (Pictet and Genequand, Abstr., 1902, i, 584) on ψ -trimethylbrazilone (the isomeride obtained by the action of sulphuric acid on trimethylbrazilone) in cooled glacial acetic acid solution leads to the formation of *nitro- ψ -trimethylbrazilone*, $C_{16}H_8O_3(OMe)_3 \cdot NO_2$, which separates from ethyl acetate in yellowish-brown crystals, melts at $210-214^{\circ}$, is sensitive to light, and when boiled with acetic anhydride and sodium acetate yields a *product*, probably *nitro- β -acetyltrimethyldehydrobrazilin*, $C_{18}H_8O_3(OMe)_3 \cdot NO_2$, forming glistening, yellow crystals and not melting at 260° .

When nitrated in the same manner, the monomethyl ether of ψ -trimethylbrazilone yields the *nitro-derivative*, $C_{16}H_7O_2(OMe)_4 \cdot NO_2$, which crystallises from alcohol, melts at $196-198^{\circ}$, and does not react with diazomethane.

When treated with twice its weight of diacetylorthonitric acid in 10 vols. of glacial acetic acid, ψ -tetramethylhæmatoxyline (the isomeride of tetramethylhæmatoxyline) yields a mononitro-derivative, $C_{16}H_7O_3(OMe)_4 \cdot NO_2$, which crystallises in long, glistening, yellow needles and melts at $221-222^{\circ}$. On acetylation this yields a *dehydroacetate*, $C_{18}H_7O_3(OMe)_4 \cdot NO_2$, which crystallises in long, sulphur-yellow needles and melts at $198-200^{\circ}$, together with a small amount of a sparingly soluble *isomeride*, which crystallises in slender, light yellow needles, melts and decomposes at $289-291^{\circ}$, has a low specific gravity, and is formed on treatment of the product melting at $198-200^{\circ}$ with acetic anhydride and sulphuric acid.

Nitration of ψ -tetramethylhæmatoxyline with four times its weight

of diacetylorthonitric acid in four vols. of cooled glacial acetic acid leads to the formation of the *dinitro*-derivative, $C_{16}H_6O_3(OMe)_4(NO_2)_2$, which forms yellow crystals, melts and decomposes at $173-176^\circ$, and yields a *dehydroacetyl* derivative, $C_{18}H_6O_3(OMe)_4(NO_2)_2$; this crystallises in slender, yellow needles and melts and decomposes at $266-268^\circ$.

Nitration of the methyl ether of ψ -tetramethylhæmatoxylone by means of diacetylorthonitric acid, leads to the formation of three isomeric *mononitro*-derivatives, $C_{16}H_6O_3(OMe)_5 \cdot NO_2$; the isomeride melting at $131-136^\circ$ forms slender, yellow crystals and is prepared also by the action of diazomethane on nitro- ψ -tetramethylhæmatoxylone; the second melts at $162-165^\circ$ and forms short, slender, yellow needles, whilst that melting at $206-207^\circ$ crystallises in long, slender, yellow needles.

G. Y.

Yellow Colouring Matter in Surinam Greenheart. W. H. BLOEMENDAL (*Chem. Centr.*, 1906, ii, 527; from *Pharm. Weekblad*, 1906, 43, 678-686).—In the author's opinion, the dyes variously described as Tecomin, Grönhartin, Bethabarra colouring matter, Taigu-Lapachoic acid, and Lapachol are all identical with the yellow, crystalline substance of the formula $C_{15}H_{14}O_3$, obtained from the wood of the *Bignonia* and described first by Paterno and later by Hooker (*Trans.*, 1896, 69, 1355).

P. H.

Colouring Matters of Phæophyceæ. M. TSWETT (*Chem. Centr.*, 1906, ii, 529-530; from *Ber. Deut. bot. Ges.*, 1906, 24, 235-244).—The production of the brown substance, phycophæin, is attributed to the oxidation of colourless chromogen. The following properties are mentioned as characteristic of carotin; unlike the xanthophylls or fucoxanthin it is more soluble in light petroleum, benzene, or carbon disulphide than in strong alcohol and is not adsorbed from a light petroleum solution by powdered calcium carbonate; moreover, neither the crystallised substance nor an alcoholic solution is turned blue by hydrochloric acid, and a solution in light petroleum shows three absorption bands, two at $492-475 \mu\mu$ and one at $460-445 \mu\mu$. In addition to carotin and fucoxanthin, the author has isolated from fucus extract a substance, *fucoxanthophyll*, which closely resembles fucoxanthin in its solubilities and its spectroscopic behaviour, but optical properties of which remain unchanged by treatment with sodium hydroxide. Chlorophyllin γ , which is also contained in the seaweed, is insoluble in light petroleum, but is soluble in alcohol or ether; when dissolved in the latter solvent, it shows absorption bands at $638-622 \mu\mu$, $588-575 \mu\mu$, and $465-440 \mu\mu$. The natural brownish-green colour of algæ is produced as a result of the mixture of all the above-mentioned colouring matters. The destruction of the fucoxanthin is the cause of algæ turning green.

P. H.

[**Action of Formaldehyde on Gallocyanin.** FARBERWERKE VORM. L. DURAND, HUGUENIN & Co. (D.R.-P. 171459).—Gallocyanin and formaldehyde condense to form a new colouring matter which is readily reduced with reducing agents such as zinc dust and hydro-

chloric acid, sodium hyposulphite or sodium sulphide to form a new leuco-base, which is obtained in the form of grey or yellow hydrochloride. This salt dissolves in water to a brownish-yellow solution; in concentrated sulphuric acid, it exhibits a blue-reddish-yellow dichroism. The leuco-base is precipitated by alkalis as a greenish-yellow, flocculent precipitate, which oxidises on exposure to air. The addition of manganese dioxide to an acid solution of the leuco-base develops an intense greenish-blue coloration. The leuco-base dyes wool in an acid bath.

G. T. M.

Conjugated Dionium Ring Systems. HERMAN DECKER (*Ber.*, 1906, **39**, 3069—3071. Compare Abstr., 1905, i, 667).—Attention is called to the facility with which certain cyclic complexes of high molecular weight undergo a reversible process of oxidation and reduction. Dinaphthylene dioxide dissolves in concentrated sulphuric acid to a light yellow solution in the absence of oxygen. In the presence of this or other oxidising agent, the colour changes to dark blue, due to the dioxonium salt (compare Bünzly and Decker, Abstr., 1905, i, 884). A small quantity of water added to the yellow solution precipitates the original compound, but larger quantities can be added to the blue solution, changing its colour first to red (carbinolmonoxonium salt), and then precipitating the yellow dicarbinol base. The blue solution is readily changed by reducing agents to the yellow, fluorescent solution of dinaphthylene dioxide.

Similar relations have been observed between isologous coeroxene and between coerthiene derivatives (compare this vol., i, 687).

C. S.

Researches on Furans. 2:5-Dicarbethoxy-3:4-diketotetrahydrofuran. I. TREAT B. JOHNSON and CARL O. JOHNS (*Amer. Chem. J.*, 1906, **36**, 290—294).—*Ethyl 3:4-diketotetrahydrofuran-2:5-dicarboxylate*, $O \begin{array}{l} \text{CH}(\text{CO}_2\text{Et}) \cdot \text{CO} \\ \text{CH}(\text{CO}_2\text{Et}) \cdot \text{CO} \end{array}$, obtained in quantitative yield by

the condensation of ethyl oxalate with ethyl diglycollate, forms stout, prismatic crystals, melts at 189°, and is very soluble in hot alcohol; the sodium salt is obtained as a white powder.

E. G.

Rhodamines. II. EMILIO NOELTING and KARL DZIEWOŃSKI (*Ber.*, 1906, **39**, 2744—2749. Compare Abstr., 1905, i, 935).—*Tetraethylrhodamine silver nitrate*, $\text{C}_{28}\text{H}_{30}\text{O}_3\text{N}_2 \cdot \text{AgNO}_3$, obtained by mixing alcoholic solutions of the components, crystallises in glistening, bluish-green plates. *aporoRhodamine* forms a similar compound which is decomposed when shaken with cold water.

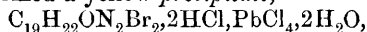
The esters of aporhodamine are prepared readily by the usual catalytic method, using hydrogen chloride. *Ethylaporhodamine hydrochloride*, $\text{C}_{25}\text{H}_{24}\text{O}_3\text{NCl} \cdot 5\text{H}_2\text{O}$, crystallises in pale red needles with a golden lustre, melts at 95°, and is not hydrolysed by boiling water. When decomposed by aqueous solutions of alkalis, the hydrochloride yields *aporhodamine*, but with the theoretical amount of cold alcoholic potassium hydroxide, it yields the *carbinol ether* of the

ester, $O \begin{smallmatrix} \text{C}_6\text{H}_3\text{Me} \\ \text{C}_6\text{H}_3(\text{NMe}_2) \end{smallmatrix} > C(\text{OEt}) \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et}$, in the form of colourless prisms melting at 105° . With hydrochloric acid, ethyl alcohol is eliminated and the hydrochloride of the ester regenerated.

apoRhodamine-imide, $O \begin{smallmatrix} \text{C}_6\text{H}_3(\text{NMe}_2) \\ \text{C}_6\text{H}_3\text{Me} \end{smallmatrix} > C \begin{smallmatrix} \text{NH} \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CO}$, obtained by the action of hot alcoholic ammonia on the hydrochloride of the ester, crystallises in large, glistening prisms, melts at 227° , and contains a half molecule of alcohol of crystallisation. It dissolves in hot dilute acids, yielding colourless solutions. J. J. S.

Compounds of the Hydrochlorides of the Alkaloids with the Chlorides of the Heavy Metals and the Corresponding Bromine Compounds. A. CHRISTENSEN (*J. pr. Chem.*, 1906, [ii], 74, 161—187. Compare Classen and Zahorsky, *Abstr.*, 1893, ii, 464; Wells, *ibid.*, 523; Goebbels, *Abstr.*, 1895, i, 390).—Lead tetrachloride combines with quinine hydrochloride in hydrochloric acid solution to form an amorphous *additive* compound, which gradually becomes yellow and crystalline: with cinchonidine hydrochloride forming a yellow *precipitate* consisting of small prisms, and with cinchonine hydrochloride forming a *precipitate* consisting of rosettes of microscopic, yellow needles. These three additive compounds readily decompose, yielding an odour of chlorine.

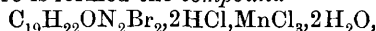
In the same manner, from α -cinchonidine dibromide hydrochloride there is formed the compound $\text{C}_{19}\text{H}_{22}\text{ON}_2\text{Br}_2 \cdot 2\text{HCl} \cdot \text{PbCl}_4 \cdot 2\text{H}_2\text{O}$, which is obtained in yellow, microscopic prisms and does not decompose when dried. The precipitate formed from β -cinchonidine dibromide hydrochloride is amorphous. With α -cinchonine dibromide hydrochloride there is formed a yellow *precipitate*,



which consists of concentric aggregates of microscopic needles; the *precipitate* formed with β -cinchonine dibromide hydrochloride is yellow and amorphous.

The action of potassium bromide solution on the freshly-prepared double salt of α -cinchonidine dibromide hydrochloride and lead tetrachloride leads to the formation of a *product* which crystallises in quadratic, yellow leaflets or prisms, and when treated with water yields lead bromide. The *product* of the action of lead bromide and bromine on β -cinchonidine dibromide in hydrobromic acid solution behaves as a mixture of the compounds $\text{C}_{19}\text{H}_{22}\text{ON}_2\text{Br}_2 \cdot 2\text{HBr} \cdot \text{PbBr}_4$ and $\text{C}_{19}\text{H}_{22}\text{ON}_2\text{Br}_2 \cdot 2\text{HBr} \cdot \text{Br}_2$.

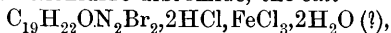
Double salts of manganese trichloride (compare Rice, *Trans.*, 1898, 73, 258; Meyer and Best, *Abstr.*, 1900, ii, 77) were prepared by adding a solution of the alkaloid in glacial acetic acid solution to manganese dioxide stirred into glacial acetic acid, and adding the calculated amount of 40 per cent. hydrochloric acid or passing hydrogen chloride into the mixture. With α -cinchonidine dibromide hydrochloride there is formed the *compound*



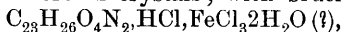
which forms green, microscopic crystals, decomposes and becomes brown on addition of water, and reacts with potassium iodide and hydro-

chloric acid, yielding the periodide. The similarly-constituted *salt* with β -cinchonidine dibromide hydrochloride contains H_2O , is obtained as a light green powder consisting of concentric aggregates of small crystals, and when exposed to air decomposes rapidly losing chlorine. With α - and β -cinchonine dibromide there are formed green, amorphous, hygroscopic *precipitates*, which decompose, losing chlorine in a desiccator.

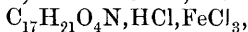
The following double salts are formed by addition of alkaloids to ferric chloride in hydrochloric acid solution (Borsbach, Abstr., 1890, 643). With quinine, the salt $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2 \cdot 2\text{HCl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$, which is obtained as a yellow, crystalline powder consisting of microscopic, hexagonal prisms; with cinchonidine, the *compound* $\text{C}_{19}\text{H}_{22}\text{ON}_2 \cdot 2\text{HCl} \cdot \text{FeCl}_3 \cdot 2\text{H}_2\text{O}$, which crystallises in microscopic, yellow prisms; with cinchonine, the *salt* $\text{C}_{19}\text{H}_{22}\text{ON}_2 \cdot 2\text{HCl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$ (?), which separates in sheaves of microscopic, yellow, rectangular crystals; with α -cinchonidine dibromide, the *salt*



which crystallises in sheaves of long needles; with strychnine, the *salt* $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2 \cdot \text{HCl} \cdot \text{FeCl}_3$, which forms a precipitate consisting of microscopic, yellowish-brown crystals; with brucine, the *salt*



which forms a heavy, greyish-brown precipitate, gradually changing into spherical crystals; with cocaine, the *salt*



which separates as a sulphur-yellow, micro-crystalline powder; with morphine, the *compound* $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N} \cdot \text{HCl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$, crystallising in sheaves of microscopic, brown needles, giving the characteristic blue coloration obtained on addition of ferric chloride to morphine, and decomposing with formation of morphine hydrochloride when recrystallised from hydrochloric acid; with caffeine, the *salt* $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4 \cdot \text{HCl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$, forming microscopic, hexagonal, short crystals; with pyridine, the *compound* $\text{C}_5\text{H}_5\text{N} \cdot \text{HCl} \cdot \text{FeCl}_3$, crystallising in yellow, pointed, tetragonal prisms; with quinoline, the *salt* $\text{C}_9\text{H}_7\text{N} \cdot \text{HCl} \cdot \text{FeCl}_3$, which crystallises in microscopic, long, pointed prisms and is readily soluble in water.

Similar double salts of the alkaloids are formed with ferric bromide and hydrobromic acid; these are less stable than the corresponding chlorine compounds and can be isolated in a state of purity only in exceptional cases. With cinchonidine, the *salt* $\text{C}_{19}\text{H}_{22}\text{ON}_2 \cdot 2\text{HBr} \cdot \text{FeBr}_3 \cdot 2\text{H}_2\text{O}$ separates as an orange-red, crystalline precipitate; the cinchonine *salt* is thrown down as an amorphous precipitate, changing gradually into small, yellow prisms; the quinine *salt* is obtained as a red, amorphous precipitate; the caffeine *salt*, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4 \cdot \text{HBr} \cdot \text{FeBr}_3 \cdot \text{H}_2\text{O}$, forms a reddish-brown, micro-crystalline powder; the quinoline *salt*, $\text{C}_9\text{H}_7\text{N} \cdot \text{HBr} \cdot \text{FeBr}_3$, separates in reddish-brown, microscopic, hexagonal crystals. G. Y.

Clavine, a New Constituent of Ergot. ERNST VAHLEN (*Chem. Centr.*, 1906, ii, 690; from *Arch. exper. Path. Pharm.*, 55, 131—163).—*Clavine*, $\text{C}_{11}\text{H}_{22}\text{O}_4\text{N}_2$, is obtained when an aqueous extract of ergot is precipitated with a hot saturated solution of barium hydroxide, the

barium removed from the solution by carbon dioxide, and the concentrated filtrate extracted with hot alcohol. It forms elongated needles or small, nacreous, rhombic plates and melts at $262\text{--}263^\circ$ in a closed tube. When heated carefully it sublimes, forming star-shaped aggregates of small prisms. It dissolves readily in water and is not precipitated by alkali hydroxides or carbonates. It is only slightly soluble in ethyl alcohol, and insoluble in ether, ethyl acetate, or light petroleum.

In aqueous solution it is split up into two substances having approximately the same molecular weight. By addition of copper hydroxide or a solution of copper acetate, the copper salts of two acids, both containing nitrogen, are formed, one of which is soluble, the other insoluble in water.

The aqueous solution of clavine has an insipid taste and yields no precipitate with the alkaloid reagents. It is much more soluble in acid and alkaline solutions than in water. On evaporation of a hydrochloric acid solution, delicate prisms of the *hydrochloride*, $\text{C}_{11}\text{H}_{22}\text{O}_4\text{N}_2 \cdot 2\text{HCl}$, are obtained. It exerts a specific action on the uterus causing this to contract.

H. M. D.

Morphine. VIII. Trihydroxyphenanthrene from Hydroxycodine. LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1906, 39, 3252—3255).—The methoxydiacetoxyphenanthrene obtained from hydroxycodine (compare Knorr and Schneider, this vol., i, 449) is oxidised by chromic and glacial acetic acids to Vongerichten's acetyl-methylmorpholquinone (*Abstr.*, 1898, i, 281). From this it follows that the hydroxyl group, introduced into codeine by oxidation, must be situated in position 9 or 10, and, moreover, that as this hydroxyl group exhibits an alcoholic and not a phenolic function, consequently the "bridge" carbon atoms of the phenanthrene nucleus, not only in codeine, but also in methylmorphimethine, must be dihydrogenated. This result renders untenable Freund's formulæ for thebaine and codeine (*Abstr.*, 1905, i, 918; this vol., i, 303) and Pschorr's "pyridine" formula for morphine (*Abstr.*, 1903, i, 193).

Methoxydiacetoxyphenanthrene has been obtained by Pschorr from dichloromethylmorphimethine (see following abstract).

C. S.

Halogen Derivatives of Morphine and Codeine, and their Degradation. ROBERT PSCHORR (*Ber.*, 1906, 39, 3130—3139).—[With HERMANN VOGTHER.]—*Chloromorphide*, $\text{C}_{17}\text{H}_{18}\text{O}_2\text{NCl}$, resulting from the action of hydrogen chloride on morphine at the ordinary temperature, melts at 192° (corr.); the *methiodide*, $\text{C}_{17}\text{H}_{18}\text{O}_2\text{NCl} \cdot \text{MeI}$, melts at 207° (corr.).

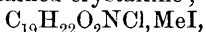
Bromomorphide hydrobromide, $\text{C}_{17}\text{H}_{18}\text{O}_2\text{NBr} \cdot \text{HBr}$, obtained by treating morphine with phosphorus pentabromide and subsequently with hydrogen bromide, decomposes at 196° ; the *base*, $\text{C}_{17}\text{H}_{18}\text{O}_2\text{NBr}$, forms needles and melts at 170° , the *methiodide* at 200° , and the *anilino-carboxylic ester*, $\text{C}_{24}\text{H}_{23}\text{O}_3\text{N}_2\text{Br}$, at 204° .

Bismorphide, $(\text{C}_{17}\text{H}_{18}\text{O}_2\text{NS})_2$, is prepared by heating chloro- or bromo-morphide with alcoholic potassium hydrosulphide; it melts at 201° and forms a *methiodide*, $(\text{C}_{19}\text{H}_{23}\text{O}_2\text{NSI})_2$, which melts at 253° and

is also obtained from *bisthiocodide*, $(C_{18}H_{20}O_2NS)_2$, which is soluble in alkali and melts at 200° (corr.). *Ethylthiocodide*, $C_{20}H_{25}O_2NS$, obtained by heating bromocodide with alcoholic sodium mercaptide in an atmosphere of hydrogen, melts at 145° (corr.).

[With E. KUI TZ and HEINRICH ROTH.]—*Chlorocodide methiodide*,
 $C_{19}H_{23}O_2NCl$,

decomposes at 166 — 167° and does not yield chloromethylmorphimethine by heating with sodium hydroxide. The *hydrochloride* of the chlorinated methine base, $C_{19}H_{22}O_2NCl \cdot HCl$, results, however, when α -methylmorphimethine is treated with phosphorous chloride in chloroform; it crystallises in tufts of needles and melts at 177 — 178° (corr.). The base has not been obtained crystalline; the *methiodide*,

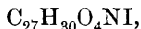


forms slender needles and melts at 163° (corr.). In the absence of a solvent, the preceding reaction results in the formation of the compound $C_{19}H_{22}O_2N \cdot O \cdot P(OH)_2 \cdot HCl$.

By heating with acetic anhydride, chloromethylmorphimethine hydrochloride yields Knorr's acetylmethyldihydroxyphenanthrene (Abstr., 1889, 905). The nitrogenous fission product is, according to the conditions of the decomposition, either methyl- β -hydroxyethylamine or dimethyl- β -hydroxyethylamine and a base having the composition of tetramethylethylenediamine.

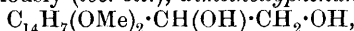
Dichloromethylmorphimethine, $C_{19}H_{23}O_3NCl_2$, obtained as the hydrochloride by the action of phosphoric chloride on α -methylmorphimethine in chloroform, decomposes at 180 — 181° and forms a crystalline *methiodide* which decomposes at 153 — 154° . The decomposition of the base by acetic anhydride yields the same basic products as the monochloro-compound, and 3-methoxy-4 : 9-(or 4 : 10)-diacetoxyphenanthrene. The latter substance, which has been obtained by Knorr by the degradation of hydroxycodine, has its constitution partially determined by its oxidation to 4-acetoxy-3-methoxyphenanthraquinone.

Benzoylcodine methiodide, $C_{26}H_{28}O_4NI$, melts at 254° (corr.). *Benzoyl- α -methylmorphimethine* melts at 182 — 183° , and its *methiodide*,



at 188° . Codeine yields with phenylcarbimide the *anilinocarboxylic ester*, which melts at 141° ; the *methiodide*, $C_{26}H_{29}O_4N_2I$, at 141° . The corresponding compound of α -methylmorphimethine melts at 122 — 123° , and its *methiodide* at 251° (corr.). C. S.

Constitution of apoMorphine. ROBERT PSCHORR [and WALTHER KARO] (*Ber.*, 1906, 39, 3124—3128. Compare Abstr., 1903, i, 193).—The methylation of *apomorphine* by methyl sulphate instead of by diazomethane leads to the ultimate formation of dimethoxyvinylphenanthrene in quantitative yield. When the latter is oxidised rapidly in acetone by potassium permanganate, there is formed, in addition to the acid described previously (*loc. cit.*), *dimethoxyphenanthrylglycol*,



which forms glistening leaflets and melts at 145° (corr.); the *acetate*, $C_{22}H_{22}O_6$, melts at 126 — 127° (corr.).

Pentabromodimethoxyvinylphenanthrene, $C_{15}H_{13}O_2Br_5$, resulting by

the bromination of the tribromo-compound (*loc. cit.*), melts at 153—154° (corr.).

By distillation with zinc dust, dimethylapomorphimethine or dimethoxyvinylphenanthrene yields two *ethylphenanthrenes*, α and β . The former is volatile with steam, melts at 109—110°, and forms a *picrate*, $C_{16}H_{14}C_6H_3O_7N_3$, which melts at 138—140° (corr.), and a *quinone* which melts at 187—188° (corr.).

The β -compound crystallises in needles and melts at 172—173° (corr.). The nitrogenous products of the distillation are hydrogen cyanide, ammonia, and trimethylamine.

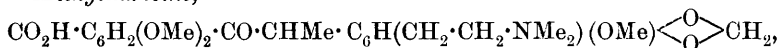
C. S.

Narceine. I. Alkylnarceines and Alkylhomonarceines.

RUDOLPH TAMBACH and CARL JAEGER (*Annalen*, 1906, **349**, 185—200. Compare Freund and Frankforter, *Abstr.*, 1894, i, 58).—The sodium salt of narceine melts at 163—165°.

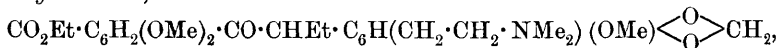
When boiled together in absolute alcoholic solution, narceine and methyl sulphate form an additive compound, which crystallises from alcohol in rhomboids or from water in slender needles, and melts at 200—201°.

Methylnarceine,



is formed by treating narceine with the calculated amounts of *N*-sodium hydroxide and methyl sulphate; it melts and decomposes at 266°; the *hydrochloride*, $C_{24}H_{29}O_8N \cdot HCl$, crystallises from alcohol and melts at 243°; the *sodium* derivative crystallises in nacreous, glistening leaflets and is readily soluble in water or alcohol; the *platinichloride* forms yellow leaflets and melts at 209—210°.

Ethylnarceine, prepared by the action of ethyl sulphate on narceine in sodium hydroxide solution, melts at 175—177°; the *hydrochloride*, $C_{25}H_{31}O_8N \cdot HCl$, melts at 231°; the *platinichloride* melts at 174°. When heated with alcoholic hydrogen chloride, the base forms *ethyl narceine*,



which is isolated as the *hydrochloride*, $C_{27}H_{35}O_8N \cdot HCl$, melting at 218.5—219°; the *platinichloride* melts at 220°.

The alkylnarceines may be prepared by the action of alkyl haloids instead of the alkyl sulphates on narceine in alcoholic sodium or potassium hydroxide instead of *N*-sodium hydroxide solution or on sodium narceine.

The alkali salts of narceine react with 2 mols. of methyl sulphate in alcoholic solution, forming an *additive* compound of methylnarceine and methyl sulphate,

$CO_2H \cdot C_6H_2(OMe)_2 \cdot CO \cdot CHMe \cdot C_6H(C_2H_4 \cdot NMe_3 \cdot SO_4Me)(OMe) : O_2 : CH_2$, which is formed also by the action of methyl sulphate on methylnarceine in alcoholic solution; it melts at 184—186° and is soluble in alcohol.

The authors have repeated part of Freund's experiments (*loc. cit.*). The action of methyl iodide on narceine in boiling ethyl-alcoholic

potassium hydroxide, or on sodium narceine in boiling methyl or ethyl alcohol, or on methylnarceine at 110—120°, leads to the formation of methylnarceinium methiodide melting at 207—209°. The action of ethyl iodide on sodium narceine in boiling ethyl-alcoholic solution or in the absence of a solvent, leads to the formation of ethyl-narceinium ethiodide; methylnarceine was not obtained by the action of methyl alcohol on sodium narceine. The alcohol takes no part in the reaction.

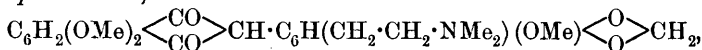
Ethylnarceinium methiodide, formed by heating ethylnarceine with methyl iodide, melts at 209—211° or, when mixed with methyl narceinium methiodide, at 200°. *Ethyl narceinium ethiodide*, prepared from ethylnarceine and ethyl iodide, crystallises in sheaves of large needles, melts at 191—193°, and forms a yellow precipitate when treated with sodium hydroxide in aqueous solution.

Methylhomonarceine, prepared by treating homonarceine with methyl sulphate and sodium hydroxide, is isolated as the *hydrochloride*, which crystallises in sheaves of prisms and melts and decomposes at 230—231°; the *platinichloride* melts at 181—182°.

Ethyl methylhomonarceine hydrochloride, prepared by boiling the preceding substance with alcoholic hydrogen chloride, melts at 212°, and gives an intense yellow coloration with aqueous sodium hydroxide; the *platinichloride* melts at 217—218°.

Ethylhomonarceine, prepared from homonarceine, ethyl sulphate, and *N*-sodium hydroxide, is isolated as the *hydrochloride*, melting and decomposing at 212°; the *platinichloride* melts at 152—155°.

apoNarceine,



is prepared by heating narceine with phosphorus oxychloride; it crystallises from alcohol, melts at 112—115°, is readily soluble in hot alcohol, but only sparingly so in water, and is insoluble in aqueous alkali hydroxides. The *hydrochloride*, $\text{C}_{23}\text{H}_{25}\text{O}_7\text{N} \cdot \text{HCl} \cdot \text{H}_2\text{O}$, is an intense canary-yellow, melts at 144°, and is hydrolysed by boiling aqueous sodium hydroxide. G. Y.

Constitution of Histidine. ADOLF WINDAUS and FRANZ KNOOP (*Beitr. chem. Physiol. Path.*, 1906, 8, 406—408. Compare Abstr., 1905, i, 834).—According to Niementowski (*Ber.*, 1899, 32, 1460; compare O. Fischer, Abstr., 1901, i, 413), the rupture of an iminazole ring by the action of benzoyl chloride is by no means general, and hence Fränkel's criticism (this vol., i, 547) of the authors' iminazole formula for histidine has little value.

Potassium hydroxide and benzenesulphonic chloride, or naphthalene sulphonic chloride, do not rupture the ring in methyliminazole. The histidinecarboxylic acid described by Fränkel melts at 209° (corr.), and not at 195°, and is identical with the glyoxaline-4-carboxylic acid previously described by the authors. J. J. S.

Erlenmeyer, jun.'s, Brucine Cinnamates. WILLY MARCKWALD and RICHARD METH (*Ber.*, 1906, 39, 2598—2600. Compare Erlenmeyer, jun., Abstr., 1905, i, 892; this vol., i, 21, 176; Erlen-

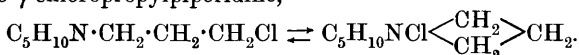
meyer, jun., and Barkow, this vol., i, 429; Marekwald and Meth, this vol., i, 360, 585).—The authors consider that Erlenmeyer, jun.'s, conclusions regarding the stereoisomeric cinnamic acids are erroneous. The optically inactive salt, described by Erlenmeyer as having been obtained from naturally occurring cinnamic acid and brucine, and sometimes also from the synthetical acid and brucine, is obtained by the authors by the combination of cinnamic acid (2 mols.) and brucine (1 mol.). The salt $C_{23}H_{26}O_4N_2 \cdot (C_9H_8O_2)_2$ melts at 135° , as Erlenmeyer found, but is not quite inactive, a 1 per cent. solution of it giving $\alpha_D - 5'$ in a 2-dcm. tube.

A. MCK.

Preparation of Sodium Theobromine Formate. F. HOFFMANN, LA ROCHE & CIE. (D.R.-P., 172932).—The double salt, *sodium theobromine formate*, $NaC_7H_7O_2N_4 \cdot HCO_2Na \cdot H_2O$, is prepared by mixing aqueous solutions containing molecular proportions of pure sodium theobromine and anhydrous sodium formate; the solution is evaporated to dryness on the water-bath, when the product is obtained as a white powder of bitter taste. This substance is employed therapeutically, and has a powerful diuretic action.

G. T. M.

Tertiary and Quaternary Bases from Piperidine. SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1906, 39, 2875—2888. Compare Gabriel and Stelzner, *Abstr.*, 1896, i, 702; Hörlein and Kneisel, this vol., i, 458).— γ -Chloropropylpiperidine is transformed into a quaternary salt when evaporated with water, but if the heating is continued in order to drive off all the water, the quaternary salt is transformed back into γ -chloropropylpiperidine,



When the pure quaternary salt is distilled with 50 per cent. potassium hydroxide solution until the distillate is no longer alkaline, the chief product is a *base*, $C_{16}H_{32}ON_2$, distilling at 336 — 339° . No neutral products and no piperidine, allylpiperidine, or trimethylenedipiperidine appear to be formed. These products could not be isolated when the crude chloride containing unaltered γ -chloropropylpiperidine was used.

The base $C_{16}H_{32}ON_2$ yields an *aurichloride* melting at 131 — 132° , a *platinichloride*, $C_{16}H_{34}ON_2PtCl_6$, which sinters at 220° , and melts and decomposes at 223 — 224° , a *picrate* melting at 150 — 151° , a *hydrochloride* in the form of a crystalline, hygroscopic powder melting at 220 — 221° , and a *hydriodide* in colourless rhombs melting at 135 — 136° . The same base is obtained when trimethylenepiperidinium hydroxide is heated with water at 50° ; it is represented as *dipiperidinodipropyl ether*, $O(CH_2 \cdot CH_2 \cdot CH_2 \cdot NC_5H_{10})_2$.

The base reacts with methyl iodide, yielding a *dimethiodide*,



which melts at 165 — 168° after sintering at 140° . The corresponding *platinichloride*, $C_{18}H_{38}ON_2PtCl_6$, melts and decomposes at 244° , and the *aurichloride* melts at 164 — 165° after sintering at 155° . When heated with hydrochloric acid at 150° , the base yields γ -chloropropylpiperidine hydrochloride, and when boiled with hydriodic acid

γ -iodopropylpiperidine hydriodide. The *picrate* of γ -iodopropylpiperidine sinters at 95° and melts at 99 — 100° .

γ -Methoxypropylpiperidine, $C_5H_{10}N \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OMe$, obtained by the action of α -chloropropyl methyl ether on piperidine, is an oil distilling at 199 — 203° under 766 mm. pressure. It dissolves readily in water, and the solution has a distinctly alkaline reaction. The *aurichloride* crystallises in golden-yellow, hexagonal plates, melting at 68 — 69° . When boiled for a short time with hydriodic acid, the base yields γ -iodopropylpiperidine hydriodide.

Trimethylenedipiperidine and trimethylene bromide were condensed in the hope of obtaining the bromide of the octocyclic base described by Hörlein and Kneisel, but without result. J. J. S.

Reduction of *o*-p-Dinitrophenylpiperidine. LEOPOLD SPIEGEL and A. UTERMANN (*Ber.*, 1906, **39**, 2631—2638).—Since substances of the aminophenylpiperidine class are of pharmacological interest, the authors describe several new compounds prepared from *o*-p-dinitrophenylpiperidine by a modification of Lellmann and Geller's method (*Abstr.*, 1888, 1107). Whilst Lellmann and Geller obtained from the dinitro-compound in question substances containing chlorine, the authors by variation of the conditions obtain *o*-p-diaminophenylpiperidine and also *o*-amino-*p*-nitrophenylpiperidine. The position of the nitro-group in the latter substance was determined by transformation into *p*-nitrophenylpiperidine by means of the diazo-reaction. By the reduction of the dinitro-compound in alcoholic solution with ammonium sulphide, a small amount of *p*-amino-*o*-nitrophenylpiperidine was also obtained.

o-p Dinitrophenylpiperidine was prepared by adding piperidine (2 mols.) to an alkaline solution of chloro-2:4-dinitrobenzene, keeping the temperature below 45° , and then boiling until the solution was complete.

o-p-Diaminophenylpiperidine, $C_5H_{10}N \cdot C_6H_3(NH_2)_2$, prepared by the reduction of *o*-p-dinitrophenylpiperidine by stannous chloride, separates from light petroleum in prisms and melts at 76° . Its *hydrochloride* forms transparent needles and melts indefinitely at 225° .

Diacetyl-o-p-diaminophenylpiperidine *hydrochloride* separates from a mixture of alcohol and ether in needles and melts at 245° . *Diacetyl-o*-p-diaminophenylpiperidine separates from alcohol or light petroleum in grey leaflets and melts at 183° .

Piperidino-m-phenylenediurethane, $C_5H_{10}N \cdot C_6H_3(NH \cdot CO_2Et)_2$, prepared by the addition of ethyl chlorocarbonate to an ethereal solution of *o*-p-diaminophenylpiperidine, separates from a mixture of acetone and light petroleum in transparent, rhombic plates.

Piperidino m-phenylenedicarbamide, $C_5H_{10}N \cdot C_6H_3(NH \cdot CO \cdot NH_2)_2$, prepared from potassium isocyanate and *o*-p-diaminophenylpiperidine *hydrochloride*, separates from a mixture of acetone and light petroleum in stellate needles and melts at 190° .

p-Nitro-*o*-aminophenylpiperidine, $C_5H_{10}N \cdot C_6H_3(NO_2) \cdot NH_2$, prepared by the partial reduction of *o*-p-dinitrophenylpiperidine by ammonium sulphide or by stannous chloride, separates from light petroleum in prisms or pyramids and melts at 86° . Its *hydrochloride* is unstable.

4-Nitro-2-acetylaminophenylpiperidine, $C_5H_{10}N \cdot C_6H_3(NO_2) \cdot NHAc$, separates from light petroleum in yellow prisms and melts at 106° .

Piperidino-4-nitrophenyl-2-urethane, $C_5H_{10}N \cdot C_6H_3(NO_2) \cdot NH \cdot CO_2Et$, separates from a mixture of acetone and water in pale yellow needles and melts at 120° .

Dipiperidino-4-nitrophenyl-2-carbamide, $CO[NH \cdot C_6H_3(NO_2) \cdot C_5H_{10}N]_2$, prepared by the addition of a solution of phosgene in toluene to a solution of 4-nitro-2-aminophenylpiperidine in benzene, separates from a mixture of acetone and light petroleum in needles and melts at 206° .

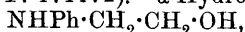
2-Nitro-4-aminophenylpiperidine, $C_5H_{10}N \cdot C_6H_3(NO_2) \cdot NH_2$, formed, together with its isomeride, by the reduction of 2:4-dinitrophenylpiperidine with ammonium sulphide, separates from light petroleum in dark red needles and melts at 112.5° .
A. McK.

*iso*Propyl-4-stilbazole, *m*-Methyl-4-stilbazole, and *m*-Methyl-2-stilbazole. HERMANN FREUND (*Ber.*, 1906, 39, 2833—2837).—*iso*Propyl-4-stilbazole, prepared by heating 4-picoline with cuminaldehyde in presence of zinc chloride, melts at 65 — 67° and forms a golden-yellow, crystalline *picrate* melting at 188 — 190° , a yellowish-white *mercurichloride* melting at 165 — 167° , and a yellow *platinichloride* melting at 191 — 193° . The *dibromide* forms reddish-yellow crystals, which sinter at 135° and melt at 144 — 146° . *iso*Propyl-dihydro-4-stilbazole is a yellow oil boiling at 185 — 195° under 35 mm. pressure; the *aurichloride* melts at 116 — 117° .

m-Methyl-4-stilbazole is a colourless oil distilling between 220° and 225° under 35 mm. pressure; the *picrate* forms yellow crystals, melting at 194 — 196° ; the *aurichloride* sinters at 158° and melts at 166 — 168° ; the *platinichloride* melts between 194° and 195° , and the *dibromide* at 125 — 127° . *m*-Methyldihydro-4-stilbazole is a colourless liquid, boiling at 220° under 60 mm. pressure; the *picrate* melts at 122 — 124° , the *platinichloride* at 171 — 172° . *m*-Methyl-4-stilbazoline is a viscous, reddish-yellow oil, distilling at 200° under 50 mm. pressure.

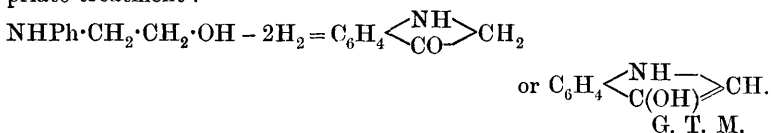
m-Methyl-2-stilbazole is a light, mobile oil, boiling at 220° under 45 mm. pressure; the *picrate* melts at 214 — 215° ; the *aurichloride* forms needles melting at 135 — 136° ; the *platinichloride* melts at 186 — 187° ; the *dibromide* melts at 145 — 146° . *m*-Methyldihydro-2-stilbazole is a colourless oil, boiling at 220° under 35 mm. pressure; the *picrate* melts at 131 — 132° , the *aurichloride* at 79 — 80° , and the *platinichloride* at 156 — 157° . *m*-Methyl-2-stilbazoline is a light oil, distilling at 195 — 197° under 35 mm. pressure.
E. F. A.

Preparation of Indoxyl and its Derivatives. BADISCHE ANILIN-UND SODA-FABRIK (D.R.-P. 171172).— α -Hydroxyethylaniline,



its homologues, alkali derivatives, carboxylic acids, or the *N*-alkyl derivatives of the foregoing substances when fused with alkali metals, alkali amides, alkali hydroxides, or mixtures of these with the oxides

of the alkaline earth metals, furnish indoxyl and indigotin on appropriate treatment :



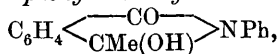
A New Indolenine Base. DUŠAN J. GRGIN (*Monatsh.*, 1906, 27, 731—742. Compare Plancher, *Abstr.*, 1898, i, 536 ; Brunner, *Abstr.*, 1900, i, 360).—*p*-Tolyldihydrazine reacts with isobutaldehyde at 60°, forming water and 3 : 3 : 5-trimethylindolenine, which is isolated as the zincchloride, $(\text{C}_{11}\text{H}_{13}\text{N})_2\text{ZnCl}_2$; this crystallises from alcohol in almost white leaflets and melts at 208—209°. The base, $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \text{CMe}_2 \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{CH}$, boils at 198—200° under 30 mm. pressure, crystallises with difficulty in almost colourless leaflets, melts at 142—143°, or, in consequence of polymerisation, after four and a half days in a vacuum at 156—157°, or after twenty days at 172—173°. The base melting at 172—173° forms with silver nitrate a precipitate, $(\text{C}_{11}\text{H}_{13}\text{N})_2 \cdot \text{C}_{11}\text{H}_{12}\text{NAg}$, which is sensitive to light; the base melting at 142—143° does not form a precipitate with silver nitrate. The picrate, $\text{C}_{11}\text{H}_{13}\text{N} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, crystallises in glistening, yellow prisms and melts at 169—170°; the platinichloride, $(\text{C}_{11}\text{H}_{13}\text{N})_2\text{H}_2\text{PtCl}_6$, crystallises in dark yellow prisms.

When heated with concentrated hydrochloric acid in a reflux apparatus, the indolenine base is converted into 2 : 3 : 5-trimethyl indole, which melts at 190° and forms a picrate melting at 177—180° (compare Wolff, *Abstr.*, 1889, 259).

Digestion of the indolenine base with ammoniacal silver nitrate on the water-bath leads to the formation of the corresponding indolinone, which is obtained as a white, crystalline substance, becoming brown on drying, and melting at 146°.

The action of bromine on the indolenine base in hydrochloric acid solution leads to the formation of the derivative, $\text{C}_{11}\text{H}_{12}\text{ONBr}$, which crystallises in light yellow leaflets and melts at 203—204°. G. Y.

Action of Mixed Organomagnesium Compounds on Imides. CONSTANTIN BÉIS (*Compt. rend.*, 1906, 143, 430—432. Compare *Abstr.*, 1904, i, 503, 671 ; Sachs and Ludwig, *Abstr.*, 1904, i, 266).—Phenylphthalimide reacts with nascent magnesium alkyl halides to form substituted isoindolinones, and the following compounds were thus prepared. 3-Hydroxy-2-phenyl-3-methylisoindolinone,

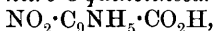


forms colourless crystals melting at 185°, and 3-hydroxy-2-phenyl-3-ethylisoindolinone, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CEt}(\text{OH}) \end{array} \text{NPh}$, colourless crystals melting at 160°. With nascent magnesium phenyl bromide, phenylphthalimide yields a mixture of 3-hydroxy-2 : 3-diphenylisoindolinone, melting at 195°, and benzoylbenzophenone, $\text{C}_6\text{H}_4(\text{COPh})_2$, melting at 149° (compare Zincke, this Journal, 1876, i, 703), separated by their difference of solubility in benzene and in alcohol. M. A. W.

Halogen Derivatives of 8-Methylquinoline and Nitro-8-quinolinealdehyde. JOH. HOWITZ and PAUL NÖTHER (*Ber.*, 1906, **39**, 2705—2713. Compare *Abstr.*, 1902, i, 397; 1905, i, 471).—The compounds described previously as 8-bromomethylquinoline and 3-bromo-8-bromomethylquinoline are in reality 8-chloromethylquinoline and 3-bromo-8-chloromethylquinoline respectively, since in the course of their preparation hydrochloric acid is employed, whereby the bromine in the side-chain is replaced almost entirely by chlorine. Pure 8-chloromethylquinoline crystallises in large, glistening plates and melts at 56°.

When the product obtained under Lang's conditions (*Diss.*, Freiburg, 1898) is dissolved in a mixture of equal volumes of concentrated sulphuric acid and water, and the solution poured into a large volume of water, 3-bromo-8-bromomethylquinoline is precipitated, whilst from the filtrate sodium hydroxide precipitates 8-bromomethylquinoline. The former, $C_9NH_5Br \cdot CH_2Br$, separates from alcohol in colourless leaflets and melts at 145°. The latter, $C_9NH_6 \cdot CH_2Br$, separates from light petroleum in long, colourless needles or prisms, melts at 84°, and forms a *hydrobromide*, $C_9NH_6 \cdot CH_2Br \cdot HBr$, which darkens at 250°, but does not melt at 320°. By nitration it yields 5-nitro-8-bromomethylquinoline, $NO_2 \cdot C_9NH_5 \cdot CH_2Br$, which forms yellow needles or prisms and melts at 116°.

5-Nitro-8-iodomethylquinoline, $NO_2 \cdot C_9NH_5 \cdot CH_2I$, obtained from the corresponding chloro-compound and potassium iodide in aqueous-alcoholic solution, forms yellow needles and melts at 142°. By oxidation with dilute nitric acid (1:1), a quantitative yield of 5-nitro-8-quinolinealdehyde, $NO_2 \cdot C_9NH_5 \cdot CHO$, is obtained, which separates from hot water in slender, white needles, melts at 146—147°, reduces ammoniacal silver solutions, and is oxidised by chromic acid in warm dilute sulphuric acid to 5-nitro-8-quinolinecarboxylic acid,



which melts at 212°.

C. S.

[Action of Alkyl Sulphates and Sulphonates on Quinoline Bases.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 170048, 170049).—The colouring matters produced by the interaction of alkylsulphonates and quinoline bases, and subsequent treatment with alkali hydroxides, are valuable sensitising compounds which are readily prepared and have favourable absorption spectra.

Quinaldine and ethyl ethanesulphonate combine additively to form an oily product which on treatment with alcoholic potash furnishes a colouring matter crystallising from ether or alcohol in green bronzy needles, and dissolving in water to a red solution.

The additive product, $C_{10}NH_9Et \cdot SO_3Ph$, of quinaldine and ethyl benzenesulphonate was obtained crystalline and melted at 105°; when treated with warm alcoholic potash it furnished a colouring matter separating in bright golden-bronzy leaflets. A similar compound was produced from quinaldine and ethyl *p*-bromotoluenesulphonate. The additive compounds obtained from ethyl *p*-toluenesulphonate and 2:6-dimethylquinoline and quinaldine melted at 120° and 134° respectively;

that from this ester and 6-bromoquinoline was oily, but all gave colouring matters on treatment with alcoholic potash.

2:7- and 2:6-Dimethylquinolines combine additively with methyl sulphate, and in the latter case a crystalline product melting at 212° was obtained. On treatment with alcoholic potash, crystalline colouring matters are produced, the compound from the 2:7-base having a steel-blue lustre, whilst that from the 2:6-isomeride separates in lustrous, dark green needles.

G. T. M.

Colouring Matters of the Quinolinium Series. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 172118).—By the action of alkalis on the alkyl halides of quinaldine bases, or mixtures of these salts of the quinaldine and quinoline bases, red colouring matters are produced which have been employed as sensitisers in photographic practice. It is now found that quite different products are obtained when the alkali acts on these bases in the presence either of formaldehyde or of substances yielding this aldehyde. A colouring matter dissolving readily in the organic solvents, and sparingly in water to intense blue solutions, is produced on treating an alcoholic solution of quinoline and quinaldine hydriodides with sodium hydroxide and formaldehyde. The new compound separates in well-defined crystals having a green metallic reflex; it can be recrystallised from boiling methyl alcohol. Similar colouring matters are obtained from the methochlorides of quinoline and quinaldine, and the reaction takes place also in aqueous or pyridine solutions.

G. T. M.

Dyeing Properties of the Condensation Products of Quinaldine with Aldehydes. EMILIO NOELTING and E. WITTE (*Ber.*, 1906, 39, 2749—2751).—Benzylidenequinaldine [2-styrylquinoline] (*Abstr.*, 1884, 336) itself is a dye, and a 3 per cent. solution of the hydrochloride yields an intense yellow colour with cotton mordanted with tannic acid. The *p*-nitro-derivative (*Bulach*, *Abstr.*, 1887, 976) gives a somewhat more greenish shade. The isomeric *o*- and *m*-nitro-compounds, piperonylidene- and nitropiperonylidene-quinaldine, give yellow shades. Dihydroxybenzylidenequinaldine (*Nencki*, *Abstr.*, 1894, i, 520), in the form of its hydrochloride, dyes wool, silk, or cotton mordanted with tannic acid orange-red. The *diacetyl* derivative, which melts at 165° , gives a yellow shade.

p-Dimethylaminobenzylidenequinaldine, $C_{19}H_{18}N_2$, crystallises from alcohol in pale yellow plates, or from benzene in brownish-yellow, flat needles melting at 177° . The *platinichloride* and *picrate* have been prepared.

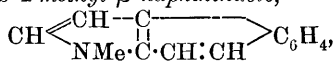
p-Aminobenzylidenequinaldine melts at 154° , and its *hydrochloride* forms pale red needles, which become deep red when dry and melt at 273° . It dyes cotton mordanted with tannic acid a brilliant red.

J. J. S.

Preparation and Hydrogenation of 1-Methyl- β -naphthindole. ROBERT PSCHORR and WALTHER KARO (*Ber.*, 1906, 39, 3140—3144).— β -Naphthylmethylamine is obtained conveniently by the methylation

of acet- β -naphthalide or of the benzenesulphonamide, followed by hydrolysis of the product. The *hydrochloride* melts at 182—183° (corr.), the *picrate* at 145° (corr.), and the *phenylcarbamide* at 133—134° (corr.).

Sodium 1-methyl- β -naphthindolesulphonate, $C_{13}H_{10}N \cdot SO_3Na$, obtained by Hinsberg's method (Abstr., 1895, i, 144), melts at 169° (corr.), and by hydrolysis yields 1-methyl- β -naphthindole,



which melts at 53° and forms a red *picrate* melting at 172—173° (corr.). By reduction of an alcoholic solution of the naphthindole by zinc and hydrogen chloride, 1-methyldihydro- β -naphthindole is obtained quantitatively; it melts at 40—41°. The *hydrochloride* melts at 205—206° (corr.), the *picrate* at 158° (corr.), the *methiodide* at 220—221° (corr.). The dihydrogenated base is converted by sodium and amyl alcohol into the *ar*-tetrahydro-compound, $C_{13}H_{17}N$, which boils at 160—180° under 14 mm. pressure, and does not form a carbonate. The *hydrochloride* melts at 186—187° (corr.), the *picrate* at 169° (corr.), the *methiodide* at 236—237° (corr.). The tertiary base is regenerated from the *picrate* by alcoholic potash at 160°.

C. S.

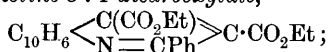
Synthesis in the Acridine Series. CARLO BAEZNER and AUGUST GARDIOL (*Ber.*, 1906, 39, 2623—2625. Compare Abstr., 1904, i, 928; this vol., i, 699, 901).—The condensation product from aniline and *o*-nitrobenzyl chloride undergoes a change similar to that of *o*-nitrobenzyl chloride itself, which, when reduced by stannous chloride in the presence of primary or secondary amines and β -naphthol, yields acridine derivatives.

When *o*-nitrobenzyl chloride and aniline are warmed together, the main product is *o*-nitrobenzylaniline, whilst phenyl *o*-dinitrobenzylamine is also produced. When *o*-nitrobenzylaniline is reduced in alcoholic solution with aluminium amalgam, it forms *o*-aminobenzylaniline, $\text{NHPh} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, which crystallises from a mixture of water and alcohol in tiny needles and melts at 81°. When condensed with β -naphthol, it forms 1 : 2-phenonaphthacridine, melting at 132°, and identical with the product which Ullmann and Baezner (Abstr., 1902, i, 694) had previously obtained from *o*-aminobenzyl alcohol and β -naphthol.

In an analogous manner, 7-hydroxy-1 : 2-phenonaphthacridine, previously obtained by Baezner (Abstr., 1904, i, 928), may be prepared from *o*-aminobenzylaniline and 2 : 7-dihydroxynaphthalene. A characteristic reaction of this compound is the behaviour of its methiodide towards ammonia when the compound $C_{18}H_{13}ON$ is formed; the latter is dark blue, is insoluble in alkali, and melts at 227°. A. McK.

Syntheses in the Quinoline Group; Phenyl-naphthaquinoline-dicarboxylic Acid and its Derivatives. LOUIS J. SIMON and CH. MAUGUIN (*Compt. rend.*, 1906, 143, 427—430).—The compound

$C_{25}H_{21}O_4N$, prepared by oxidising the cyclic compound obtained by the elimination of H_2O from the condensation product of ethyl oxalacetate and benzylidene β -naphthylamine (Abstr., 1904, i, 812), is *ethyl-2-phenyl- β -naphthaquinoline-3:4-dicarboxylate*,



it melts at 128° , can be distilled under reduced pressure at 305° , and is not changed by warming with concentrated hydrochloric or sulphuric acid or potassium hydroxide solution. The *acid*, $C_{19}H_{11}N(\text{CO}_2\text{H})_2$, obtained from the ester by prolonged heating (fifteen hours) with a 15 per cent. alcoholic solution of potassium hydroxide, forms pale yellow, microscopic needles insoluble in water or the ordinary solvents. It can be titrated in the presence of phenolphthalein, yielding the alkali salt from which the *silver*, *copper*, *lead*, *calcium*, and *barium* salts have been prepared by double decomposition. The *copper ammonium* salt,

$C_{19}H_{11}N \begin{array}{c} \text{CO}_2 \\ \text{CO}_2 \end{array} > \text{Cu} \cdot 3\text{NH}_3 \cdot 6\text{H}_2\text{O}$, forms deep blue, brilliant prisms.

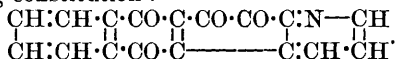
The *anhydride*, $C_{19}H_{11}N \begin{array}{c} \text{CO} \\ \text{CO} \end{array} > \text{O}$, obtained by fusing the acid at 218° , crystallises from boiling acetic acid or anhydride in golden yellow needles which melt at 218° , and yields the potassium salt of the acid by the action of aqueous or alcoholic potassium hydroxide, and the *ethyl hydrogen* ester, $\text{CO}_2\text{H} \cdot \text{C}_9\text{H}_{11}\text{N} \cdot \text{CO}_2\text{Et} \cdot \text{EtOH}$, on boiling with absolute alcohol. The same ester is also obtained when the diethyl ester is heated for five hours with a 2 per cent. alcoholic solution of potassium hydroxide; it forms massive, rhombic, highly refractive crystals of an amber-yellow colour, loses its alcohol of crystallisation at 115° , and crystallises from methyl alcohol in long, white, silky needles containing 1 mol. of methyl alcohol of crystallisation. 2-Phenyl- β -naphthaquinoline (compare Döbner and Kuntze, Abstr., 1889, 411, 412) is obtained by heating 2-phenyl- β -naphthaquinoline-3:4-dicarboxylic acid or any of its derivatives with soda lime.

M. A. W.

Syntheses in the Quinoline Group; Ethyldihydrophenyl-naphthaquinolinedicarboxylate and its Derivatives. LOUIS J. SIMON and CHARLES MAUGUIN (*Compt. rend.*, 1906, 143, 466—468. Compare preceding abstract).—The yellow compound, $C_{25}H_{23}O_4N$, melting at 146 — 147° , obtained by the elimination of H_2O from the condensation product of ethyl oxalacetate, benzaldehyde, and β -naphthylamine (Abstr., 1904, i, 812), is probably ethyl dihydrophenyl-naphthaquinolinedicarboxylate; it is not attacked by hot concentrated aqueous potassium hydroxide, but is decomposed by fusing with potassium hydroxide, yielding a mixture of 2-phenyl-naphthaquinoline, $C_{19}H_{13}N$, and 2-phenyl-naphthaquinoline-4-carboxylic acid, $C_{19}H_{12}N \cdot \text{CO}_2\text{H}$, identical with the compounds prepared by Döbner (Abstr., 1889, 411, 412). 2-Phenyl-naphthaquinoline trichloroacetate, $C_{19}H_{13}N_3 \cdot 2(\text{CCl}_3 \cdot \text{CO}_2\text{H})$, is a characteristic salt, and the *copper ammonium* salt of 2-phenyl-naphthaquinoline-4-carboxylic acid crystallises in small, blue prisms, and the *methyl* ester of the acid obtained by the action of methyl sulphate melts at 128° and is not changed by boiling with concentrated potassium hydroxide.

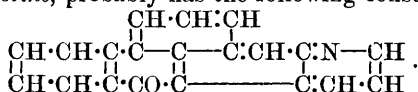
M. A. W.

Preparation of an Oxidation Product of Alizarin-blue. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 171836).—Energetic oxidation of alizarin-blue leads to the disruption of the anthraquinone nucleus and the formation of phthalic acid. When alizarin-blue in solution, or suspension in water, is treated with mild oxidising agents either in neutral or acid solution it becomes converted into a yellow compound of quinonoid character, which in all probability has the following constitution :



This substance, which is called *alizarin-blue-quinone*, is reconverted into alizarin-blue by mild reducing agents, whilst treatment with ammonia transforms it into *alizarin-blue-amide*. Chlorine, bromine, hypochlorites, manganese dioxide, lead peroxide, and dilute nitric acid may be employed as oxidising agents, but when the last of these is used the product is a salt-like compound of the ortho-quinone and the acid which evolves nitrous fumes on warming with glacial acetic acid, whilst pure alizarin-blue quinone itself separates in well-defined crystals on cooling the solution or on adding alcohol. G. T. M.

Preparation of Benzanthronequinolines. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 171939).—Although β -aminoalizarin when condensed with glycerol yields alizarin-blue, the quinoline of alizarin, yet this condensation when applied to β -aminoanthraquinone results in the formation of substances containing two new rings, $\text{C}_{14}\text{H}_9\text{O}_2\text{N} + 2\text{C}_3\text{H}_8\text{O}_3 = \text{C}_{20}\text{H}_{11}\text{ON} + 7\text{H}_2\text{O}$. The principal product, which is called *benzanthronequinoline*, probably has the following constitution :

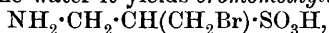


When crystallised from toluene this substance separates in well-defined yellow needles melting at 251° . Another product of this condensation which melts at $232-234^\circ$ is not homogeneous, because by fractional crystallisation it may be resolved into benzanthronequinoline, and another substance, $\text{C}_{17}\text{H}_9\text{O}_2\text{N}$, which melts at 322° and is isomeric with Graebe's anthraquinonequinoline.

Similar condensation products may be obtained from 2:6- and 2:7-diaminoanthraquinones and the sulphonic acids of the mono- and di-aminoanthraquinones. G. T. M.

Supposed Penthiazole Derivatives. SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1906, 39, 2889—2892. Compare Gadamer, *Abstr.*, 1896, i, 415; Gabriel and Hoisch, *ibid.*, 1897, i, 136).—Dixon's bromoethoxypenthiazoline (*Trans.*, 1896, 69, 31) is regarded

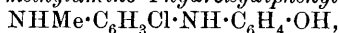
as ethoxybromomethylthiazoline, $\text{CH}_2\text{Br} \cdot \text{CH} \cdot \text{S} \begin{array}{l} \nearrow \text{C} \cdot \text{OEt} \\ \searrow \text{CH}_2 \cdot \text{N} \end{array}$, since when oxidised with bromine water it yields *bromomethyltaurine*,



which crystallises from water in rectangular plates melting and

decomposing at 273° . When reduced with zinc and sulphuric acid, the bromo-derivative yields β -methyltaurine. Bromomethyltaurine yields a *potassium* salt, $C_3H_7O_3NSBrK$, in the form of colourless, glistening plates, it dissolves readily in water, and when the solution is heated potassium bromide and *trimethyleneiminesulphonic acid*, $NH<\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}>CH\cdot SO_3H$, are formed. The latter sinters at 230° , melts at about 245 — 247° and decomposes at 255 — 263° . When boiled with hydrobromic acid, it is reconverted into bromomethyltaurine or with hydriodic acid into iodomethyltaurine. J. J. S.

[3'-Chloro-4'-methylamino-4-hydroxydiphenylamine.] CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 172079).—*p*-Aminophenol and 2-chloromethylaniline are oxidised with sodium dichromate in acid solution, when the indophenol, $NHMe\cdot C_6H_3Cl\cdot N\cdot C_6H_4\cdot O$, thus produced, separates rapidly and partly in a crystalline condition. This colouring matter dissolves in alcohol to an intense blue solution; when treated with warm sodium sulphide in alkaline solution it is reduced, yielding 3'-chloro-4'-methylamino-4-hydroxydiphenylamine,

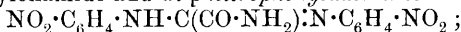


a base which melts at 105° and yields a hydrochloride crystallising in greyish-white needles. 3'-Chloro-4'-methylamino-4-ethoxydiphenylamine, $NHMe\cdot C_6H_3Cl\cdot NH\cdot C_6H_4\cdot OEt$, melts at 115° . Further action of sodium sulphide on these bases at higher temperatures leads to the production of blue sulphur colouring matters. G. T. M.

Transformations of Hydrocyanocarbodiphenylimide. GUSTAV SCHULTZ, GEORG ROHDE, and GUSTAV HERZOG (*J. pr. Chem.*, 1906, [ii], 74, 74—91).—When dissolved in concentrated sulphuric acid, hydrocyanocarbodiphenylimide gradually forms an orange-yellow solution and is regained almost quantitatively on dilution. If the solution in concentrated sulphuric acid is heated on the water-bath, the hydrocyano-compound is partially hydrolysed, yielding phenyloxamide and diphenylamidineoxamide. If the heating is prolonged, the hydrocyanocarbodiphenylimide is hydrolysed to aniline, oxalic acid, and ammonia, the aniline being partially sulphonated; only traces of isatin α -anilide are formed.

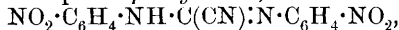
Diphenylamidineoxamide, $NHPh\cdot C(NPh)\cdot CO\cdot NH_2$, crystallises in large, glistening, yellow leaflets, melts at 155° , and, when heated above its melting point, resolidifies, forming yellow leaflets melting and decomposing at about 302° ; the solution in dilute sulphuric acid deposits phenyloxamide slowly at the ordinary temperature, but quickly if heated; when heated with aqueous sodium hydroxide, the amidineoxamide is hydrolysed, forming aniline, oxalic acid, and ammonia. On treatment with aqueous sodium nitrite in cold concentrated sulphuric acid solution, diphenylamidineoxamide yields phenyloxamide and *p*-nitrophenyloxamide, $NO_2\cdot C_6H_4\cdot NH\cdot C_2O_2\cdot NH_2$, which is formed also by the action of aqueous ammonia on ethyl *p*-nitrophenyloxamate. It crystallises from pyridine in slender, yellowish-grey needles, melts and decomposes at 308 — 310° , is stable towards acids, and is hydrolysed by aqueous alkali hydroxides, forming *p*-nitroaniline, oxalic acid, and

ammonia. *Ethyl p-nitrophenyloxamate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$, is prepared together with a *product (di-p-nitro-oxanilide?)* melting above 360° , by heating a molecular mixture of *p*-nitroaniline and ethyl oxalate in a reflux apparatus; it crystallises in almost colourless, voluminous, long needles, melts at 171° , and is hydrolysed by aqueous sodium hydroxide, forming *p*-nitroaniline, oxalic acid, and ethyl alcohol. The action of nitrogen trioxide or of nitric acid on diphenylamidinoxamide in concentrated sulphuric acid solution leads to the formation of *p*-nitrophenyloxamide and *di-p-nitrophenylamidinoxamide*,

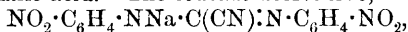


this crystallises in greenish-yellow, transparent prisms, melts and decomposes at 245° , is readily soluble in pyridine, when boiled with glacial acetic acid in a reflux apparatus yields *p*-nitrophenyloxamide, and is hydrolysed by aqueous sodium hydroxide, forming *p*-nitroaniline, oxalic acid, and ammonia.

Hydrocyanocarbodi-p-nitrophenylimide,



prepared by the action of nitric acid on hydrocyanocarbodiphenylimide in cooled concentrated sulphuric acid solution, is obtained in two modifications, of which the labile crystallises from dilute solutions in transparent, greenish-yellow, rhombic leaflets or plates, and when heated at 110° changes into the stable form; this is formed on rapid separation from a concentrated solution and crystallises in matted, thin, yellow needles. Both modifications melt and decompose at 217° , and yield *p*-nitrophenyloxamide and *p*-nitroaniline when heated with concentrated sulphuric acid at 120 — 140° ; hydrolysis by means of boiling dilute sulphuric acid leads to the formation of *p*-nitroaniline, ammonia, and oxalic acid. The *sodium* derivative,



is intensely red and yields the free nitrile when treated with dilute sulphuric acid or persistently washed with water. When heated with aqueous sodium hydroxide, hydrocyanocarbodi-*p*-nitrophenylimide yields small quantities of ammonia and *p*-nitroaniline together with a *mixture* of two substances, one of which was identified as di-*p*-nitrophenylcarbamide.

When heated with dilute sulphuric acid, hydrocyanocarbodiphenylimide yields aniline and oxanilonitrile (cyanoformanilide), which melts and decomposes at 128° (120° : Dieckmann and Kaemmerer, *Abstr.*, 1905, i, 874) and is hydrolysed by hot concentrated sulphuric acid, forming phenyloxamide.

The action of sodium nitrite on hydrocyanocarbodiphenylimide in glacial acetic acid solution leads to the formation of *nitrosocyanocarbodiphenylimide*, $\text{NO} \cdot \text{NPh} \cdot \text{C}(\text{CN}) : \text{NPh}$, which separates in stout, yellow crystals, melts and decomposes at 117 — 118° , and gives the reactions of hydrocyanocarbodiphenylimide, into which it decomposes on recrystallisation.

G. Y.

Additive Products of Derivatives of Trinitrobenzene with Certain Aromatic Nitrogen Compounds. RICCARDO CIUSA and C. AGOSTINELLI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 238—242).—The phenylhydrazones of acetone, propaldehyde, and camphor, and

probably those of all aliphatic aldehydes and ketones, readily yield crystalline picrates, the formation of which may be used for characterising small quantities of aldehydes and ketones of the aliphatic series.

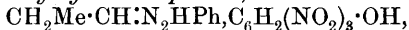
Picryl chloride reacts with propaldehydephenylhydrazone, and probably with the phenylhydrazones of all aliphatic aldehydes and ketones, yielding *s*-picrylphenylhydrazine, $R\cdot CH:N\cdot NHPh + H_2O + C_6H_2Cl(NO_2)_3 = R\cdot CHO + HCl + C_6H_2(NO_2)_3\cdot NH\cdot NHPh$. With benzalazine, piperonalazine, benzylideneaniline, and cinnamylideneaniline, a similar reaction takes place, whilst with aldehydes the corresponding trinitrophenylhydrazones are obtained according to the equation $CHR:N\cdot N\cdot CHR + H_2O + C_6H_2Cl(NO_2)_3 = HCl + R\cdot CHO + C_6H_2(NO_2)_3\cdot NH\cdot N\cdot CHR$.

With Schiff's bases, picryl chloride reacts giving the corresponding picrylanilines: $CHR:NPh + H_2O + C_6H_2Cl(NO_2)_3 = HCl + R\cdot CHO + C_6H_2(NO_2)_3\cdot NHPh$.

Acetone phenylhydrazone picrate, $CMe_2\cdot N_2HPh, C_6H_2(NO_2)_3\cdot OH$, crystallises from benzene in unstable, yellow needles melting at $81-82^\circ$.

Camphor phenylhydrazone picrate, $C_{10}H_{16}\cdot N_2HPh, C_6H_2(NO_2)_3\cdot OH$, crystallises in golden-yellow needles melting at 137° to a black liquid.

Propaldehydephenylhydrazone picrate,

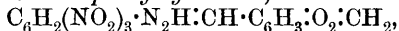


crystallises from alcohol in minute, canary-yellow needles melting at $156-157^\circ$.

The interaction of molecular proportions of propaldehydephenylhydrazone and picryl chloride in alcoholic solution yields trinitrohydrazobenzene, which melts at $186-187^\circ$ ($183-185^\circ$: Fischer, *Annalen*, 1889, 252, 2); on boiling with 90 per cent. acetic acid the latter is converted into an isomeric compound, which crystallises in golden-yellow scales melting at 186° , and probably has the structure $NH_2\cdot C_6H_4\cdot NH\cdot C_6H_2(NO_2)_3$.

Picryl chloride and benzalazine yield benzaldehydetrinitrophenylhydrazone, which melts at $273-274^\circ$; Purgotti (*Abstr.*, 1895, i, 27) gave the melting point 248° , and Curtius (*Abstr.*, 1895, i, 30) 267° .

Piperonaldehydetrinitrophenylhydrazone,



prepared by the interaction of piperonalazine and picryl chloride, separates from acetic acid in dark red crystals melting at 169° .

The action of picryl chloride on cinnamylideneaniline yields cinnamaldehyde and picrylaniline.

T. H. P.

Hydrazine Derivatives of the Diaminodiphenylmethane Series. HERMANN FINGER [with M. BAUMANN] (*J. pr. Chem.*, 1906, [ii], 74, 155-156).—The hydrazine derivatives of *pp'*-diaminodiphenylmethane and diaminoditolylmethane may be prepared by way of the diazosulphonates or the diazonium chlorides.

The *potassium diazosulphonate*, $C_{13}H_{10}O_6N_4S_2K_2$, obtained from *pp'*-diaminodiphenylmethane, separates in slender, yellow needles, and when reduced with zinc dust and boiling acetic acid, yields *pp'*-*dihydrazinodiphenylmethane*; this forms a white precipitate, crystallises from alcohol, and melts at $139-140^\circ$. The *hydrochloride*, $C_{13}H_{16}N_4\cdot 2HCl$,

forms greyish-white leaflets; the *dinitroso*-derivative is slightly yellow and melts at 88° ; the *disemicarbazide* crystallises in silvery leaflets and melts at 250° ; the *condensation* product with acetone, $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}_2)_2$, melts at $90\text{--}91^\circ$, and when reduced with zinc chloride forms a *di-indylmethane*, $\text{CH}_2\left(\text{C}_6\text{H}_5\left\langle\begin{smallmatrix}\text{CH} \\ \text{NH}\end{smallmatrix}\right\rangle\text{CMe}\right)_2$, melting at $170\text{--}175^\circ$.

pp'-Dihydrazinodiphenylmethane hydrochloride condenses with ethyl acetoacetate, forming a *product* which at 150° is converted into the corresponding *pyrazolone* melting at 210° . G. Y.

Preparation of *s*-Secondary Hydrazines from Antipyrines.

LUDWIG KNORR (*Ber.*, 1906, 39, 3265—3267).—*s*-Phenylmethylhydrazine, formed in 85 per cent. yield from antipyrine and alcoholic potash at 130° , boils at $200\text{--}201^\circ$ under 331 mm. and at 230° at the ordinary pressure; the *oxalate*, $\text{C}_7\text{H}_{10}\text{N}_2\cdot\text{C}_2\text{H}_2\text{O}_4$, forms slender needles and melts and decomposes at $155\text{--}156^\circ$.

s-Phenylethylhydrazine, obtained from 1-phenyl-3-methyl-2-ethylpyrazolone in a similar manner, boils at $237\text{--}240^\circ$ under 750 mm. pressure, and forms an *oxalate* which melts and decomposes at $167\text{--}168^\circ$.

1:2:3-Trimethylpyrazolone boils at $306\text{--}309^\circ$ under 751 mm. pressure, forms a *platinichloride* which decomposes at $197\text{--}198^\circ$, and a *picrate* which melts and decomposes at $211\text{--}212^\circ$. Alcoholic potash at 190° converts the base into *s*-dimethylhydrazine, which boils at $80\text{--}81^\circ$ under 753 mm. pressure (compare this vol., i, 817). C. S.

Crystallographic Constants of 4-Chloropyrazole. CARLO MARIA VIOLA (*Zeit. Kryst. Min.*, 1906, 42, 384—385).—Determinations are given for this substance, obtained by G. Mazzara and A. Borgo by the action of sulphuryl chloride on pyrazole. L. J. S.

Preparation of 4:6-Dioxy-2-thiopyrimidine and its 5-Alkyl Substituents.

FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 171292).—4:6-Dioxy-2-thiopyrimidine, $\text{CS}\left\langle\begin{smallmatrix}\text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO}\end{smallmatrix}\right\rangle\text{CH}_2$, was prepared by heating 4:6-di-imino-2-thiopyrimidine, $\text{CS}\left\langle\begin{smallmatrix}\text{NH}\cdot\text{C}(\text{NH}) \\ \text{NH}\cdot\text{C}(\text{NH})\end{smallmatrix}\right\rangle\text{CH}_2$, with 30 per cent. sulphuric acid.

4:6-Dioxy-2-thio-5-diethylpyrimidine, $\text{CS}\left\langle\begin{smallmatrix}\text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO}\end{smallmatrix}\right\rangle\text{CEt}_2$, was obtained in a similar manner from 4:6-diamino-2-thio-5:5-diethylpyrimidine (compare Abstr., 1905, i, 671). G. T. M.

Preparation of Barbituric Acid and its 5-Alkyl Derivatives.

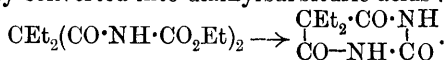
CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 171294).—Ethyl malonamate and urethane were condensed by heating on the water-bath with alcoholic sodium ethoxide, and the resulting barbituric acid precipitated from the acidified solution. The corre-

sponding *O*-alkyl derivatives were similarly prepared from the mono- and di-alkylmalonamates. G. T. M.

Preparation of 5:5-Dialkylbarbituric Acid. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 170907).—The 5:5-dialkylbarbituric acids are obtained from the corresponding thio-derivatives by heating these with solutions of the salts of the heavy metals.

Diethylthiobarbituric acid, when boiled for twenty-four to forty-eight hours with solutions of lead acetate or copper chloride, yielded a precipitate of the metallic sulphide, and the diethylbarbituric acid was then isolated on concentrating the filtered solution. G. T. M.

Preparation of 5:5-Dialkylbarbituric Acids. WILHELM TRAUBE (D.R.-P. 171992).—The diurethane derivatives of the dialkylmalonic acids are produced by heating the dialkylmalonyl chlorides with urethanes: $\text{CEt}_2(\text{COCl})_2 + 2\text{NH}_2\cdot\text{CO}_2\text{Et} = \text{CEt}_2(\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et})_2 + 2\text{HCl}$. These products, when heated at temperatures varying from 80° to 150° with metallic alkyl oxides, either alone or in alcoholic solution, are readily converted into dialkylbarbituric acids:



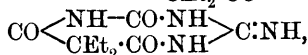
For example, 30 parts of diethylmalonylurethane, when heated with 7 to 20 parts of dry sodium ethoxide for one or two hours at 80 – 100° and then at 150° , and subsequently treated with dilute acid, yield diethylbarbituric acid melting at 191° . G. T. M.

Preparation of 5:5-Dialkylbarbituric Acids. WILHELM TRAUBE (D.R.-P. 172885, 172886. Compare this vol., i, 538, and preceding abstracts).—Instead of heating the dialkylmalonyldiurethanes with metallic alkyl oxides, the conversion of these substances into 5:5-dialkylbarbituric acids may be readily effected by heating with alcoholic or aqueous alkali hydroxides or with concentrated or fuming sulphuric acid. This transformation may likewise be carried out by the agency of aqueous or alcoholic ammonia or organic bases.

Diethylmalonyldiurethane mixed with ordinary concentrated sulphuric acid is added to fuming sulphuric acid and heated at 100° for some time. On pouring the solution into ice-cold water, 5:5-diethylbarbituric acid separates as an oil which rapidly solidifies. This acid is also formed when the diurethane is boiled with alcoholic potash, soda, ammonia, or any organic base such as guanidine, pyridine, or an alkylamine. G. T. M.

Preparation of Guanyldiethylbarbituric Acid. CHEMISCHE FABRIK VON HEYDEN AKTIEN-GESELLSCHAFT (D.R.-P. 171147).—

Guanyldiethylbarbituric acid, $\text{CO} \begin{array}{c} \text{NH}\cdot\text{CO} \\ | \\ \text{CEt}_2\cdot\text{CO} \end{array} \text{N}\cdot\text{C}(\text{NH}_2):\text{NH}$ or

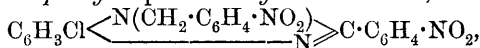


is prepared by heating together ethyl diethylmalonate and dicyanodiamidine hydrochloride in alcoholic sodium ethoxide and slightly acidifying the solution; when crystallised from hot, dilute hydrochloric acid, it separates in well-defined prisms. Prolonged boiling with

mineral acids hydrolyses the guanyl derivatives to diethylbarbituric acid. The condensation may also be effected by means of sodamide or metallic sodium. G. T. M.

Benziminazoles and their Resolution. OTTO FISCHER and FRITZ LIMMER (*J. pr. Chem.*, 1906, [ii], 74, 57—73. Compare Fischer and Hess, *Abstr.*, 1904, i, 195; Fischer, this vol., i, 539).—*p*-Chloro-dibenzylidene-*o*-phenylenediamine, $C_6H_3Cl(N:CHPh)_2$, formed from *p*-chloro-*o*-phenylenediamine and benzaldehyde at 150—170°, crystallises in colourless, nodular aggregates, melts at about 168°, and on prolonged heating above its melting point yields 6-chloro-2-phenyl-1-benzylbenziminazole, $C_6H_3Cl \left\langle \underset{N}{N(CH_2Ph)} \right\rangle CPh$, which crystallises from alcohol in white needles and volatilises at about 225°. The hydrochloride forms slender, white needles; the platinichloride crystallises in short, yellow needles; the nitrate crystallises in long, colourless prisms.

p-Chlorodi-*p*-nitrobenzylidene-*o*-phenylenediamine, prepared from *p*-chloro-*o*-phenylenediamine and *p*-nitrobenzaldehyde, crystallises in red leaflets, melts at about 150°, and gradually becomes yellow, forming 6-chloro-2-*p*-nitrophenyl-1-*p*-nitrobenzylbenziminazole,



which melts at 235°.

The product obtained on shaking *p*-chloro-*o*-phenylenediamine with ethyl acetoacetate in alcoholic solution crystallises in long, white needles, melts at 140°, forms a nitrobenzylidene derivative crystallising in reddish-yellow needles and melting at 210°, and on prolonged heating above its melting point is converted into ethyl acetate and 6-chloro-2-methylbenziminazole, $C_6H_3Cl \left\langle \underset{N}{NH} \right\rangle CMe$, which melts at 203°.

p-Chlorodiphenylquinoxaline, $C_{20}H_{13}N_2Cl$, prepared by heating a molecular mixture of *p*-chloro-*o*-phenylenediamine and benzil at 100°, crystallises in colourless, refracting leaflets, melts at 130°, and gives a red coloration with concentrated sulphuric acid.

p-Chloro-*o*-phenylenethiocarbamide, $C_6H_3Cl \left\langle \underset{NH}{NH} \right\rangle CS$, prepared by boiling *p*-chloro-*o*-phenylenediamine with a concentrated aqueous solution of ammonium thiocyanate and a small quantity of hydrochloric acid and heating the product at 130—150°, crystallises in colourless needles, melts above 270°, is almost insoluble in water, but dissolves readily in alcohol, and has a bitter taste.

p-Chloro-*o*-phenylenecarbamide, $C_6H_3Cl \left\langle \underset{NH}{NH} \right\rangle CO$, obtained by heating *p*-chloro-*o*-phenylenediamine with phosgene in toluene solution, crystallises in small, white needles, melts above 270°, and has a bitter taste.

p-Chloronitrodiacetyl-*o*-phenylenediamine, $C_{10}H_{10}O_4N_3Cl$, is prepared by adding *p*-chlorodiacyetyl-*o*-phenylenediamine, which melts at 208° (201°: Ullmann and Mauthner, *Abstr.*, 1904, i, 192) to red, fuming nitric acid; it crystallises in stellate aggregates of needles, softens at

about 240°, melts and decomposes at 245°, has weak basic and acid properties, and gives a deep red coloration with concentrated alkali hydroxides.

p-Chlorodibenzoyl-*o*-phenylenediamine, $C_{20}H_{15}O_2N_2Cl$, formed by fusing the *o*-diamine with benzoic anhydride, crystallises in soft, silky needles, melts at 230°, and is insoluble in dilute acids or alkali hydroxides. *p*-Chloronitrodibenzoyl-*o*-phenylenediamine, prepared by the action of fuming nitric acid on the preceding substance, crystallises in nodular aggregates of almost colourless needles, melts at 209–210°, dissolves in concentrated hydrochloric or sulphuric acid, and with concentrated potassium hydroxide gives a red coloration, becoming yellow on exposure to air.

6-Chloronitrobenziminazole, $NO_2 \cdot C_6H_2Cl \left\langle \begin{smallmatrix} NH \\ N \end{smallmatrix} \right\rangle CH$, prepared by dissolving 6-chlorobenziminazole (Fischer, Abstr., 1904, i, 349) in red, fuming nitric and concentrated sulphuric acids, crystallises in small, slightly yellow needles, melts at 180–181°, and is readily soluble in cold aqueous alkali hydroxides or ammonia, mineral acids, glacial acetic acid, or hot alcohol. When heated with methyl iodide and methyl alcohol in a sealed tube at 110°, it yields the quaternary iodide, $NO_2 \cdot C_6H_2Cl \left\langle \begin{smallmatrix} N(MeI) \\ NMe \end{smallmatrix} \right\rangle CH$, which crystallises in yellow prisms, and the periodide, $C_9H_9O_2N_3ClI_3$, which is obtained in blue, glistening prisms, and loses I_2 when boiled with water, or more quickly when treated with sulphur dioxide or aqueous alkali hydroxides. 6-Chloronitro-1 : 3-dimethylbenziminazolol, $NO_2 \cdot C_6H_2Cl \left\langle \begin{smallmatrix} NMe \\ NMe \end{smallmatrix} \right\rangle CH \cdot OH$, prepared by heating the quaternary iodide with an aqueous alkali hydroxide, crystallises from alcohol in yellow leaflets, becomes brown at about 190°, melts and decomposes at about 215°, and is moderately soluble in hot water. *p*-Chloronitrodimethyl-*o*-phenylenediamine, $C_8H_{10}O_2N_3Cl$, obtained on boiling the carbinol with alcoholic potassium hydroxide for half an hour, crystallises in red prisms, melts at 220°, forms a yellow ferrichloride and a hydrochloride crystallising in slender, yellow needles, regenerates the benziminazolol when boiled with concentrated formic acid, and yields 6-chloronitro-1 : 2 : 3-trimethylbenziminazole when boiled with glacial acetic acid and acetic anhydride.

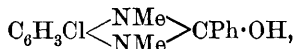
6-Chloronitro-2-methylbenziminazole, $NO_2 \cdot C_6H_2Cl \left\langle \begin{smallmatrix} NH \\ N \end{smallmatrix} \right\rangle CMe$, prepared by heating *p*-chloronitrodiacetyl-*o*-phenylenediamine with concentrated hydrochloric acid on the water-bath, or by nitrating 6-chloro-2-methylbenziminazolol, crystallises from dilute alcohol in almost colourless needles, melts at 210°, and is readily soluble in aqueous alkali hydroxides, ammonia, glacial acetic acid, or alcohol. The aurichloride forms large, golden prisms, the platinichloride, long, light-yellow needles, and the picrate, long, yellow prisms melting at 221°.

6-Chloronitro-1 : 2 : 3-trimethylbenziminazolium iodide,
 $C_{10}H_{11}O_2N_3ClI$,
 formed together with the brown, crystalline periodide when 6-chloro-

nitro-2-methylbenziminazole is heated with methyl iodide and methyl alcohol at 110° under pressure, crystallises in long, yellow needles and melts at 263° . 6-Chloronitro-1:2:3-trimethylbenziminazolol, $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Cl} \left\langle \begin{smallmatrix} \text{NMe} \\ \text{NMe} \end{smallmatrix} \right\rangle \text{CMe} \cdot \text{OH}$, prepared by gently heating the quaternary iodide with aqueous potassium hydroxide, crystallises from hot alcohol in glistening, yellow leaflets, becomes brown at about 190° , melts at about 205° , and when boiled with alcoholic potassium hydroxide is hydrolysed, yielding acetic acid and *p*-chloronitrodimethyl-*o*-phenylenediamine.

6-Chloro-2-phenylbenziminazole, $\text{C}_6\text{H}_3\text{Cl} \left\langle \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} \right\rangle \text{CPh}$, prepared by heating *p*-chlorodibenzoyl-*o*-phenylenediamine with concentrated hydrochloric acid at 160° under pressure, crystallises in glistening, colourless leaflets, melts at 210° , and is readily soluble in alcohol, hot ether, chloroform, or hot aqueous alkali hydroxides.

The quaternary iodide, $\text{C}_6\text{H}_3\text{Cl} \left\langle \begin{smallmatrix} \text{N(MeI)} \\ \text{NMe} \end{smallmatrix} \right\rangle \text{CPh}$, forms glistening leaflets, melts at 263° , and when boiled with aqueous or alcoholic potassium hydroxide is converted into the *carbinol*,



which crystallises from dilute alcohol in colourless, quadratic prisms, melts at 140° , and is only slightly hydrolysed by boiling alcoholic potassium hydroxide.

6-Chloronitro-2-phenylbenziminazole, $\text{C}_{13}\text{H}_8\text{O}_2\text{N}_3\text{Cl}$, prepared from *p*-chloronitrodibenzoyl-*o*-phenyldiamine or by nitration of 6-chloro-2-phenylbenziminazole, crystallises in yellow needles, melts at 255° , and is readily soluble in hot alcohol, glacial acetic acid, or aqueous alkali hydroxides or ammonia. 6-Chloro-2-phenyl-1:3-dimethylbenziminazolium iodide crystallises in colourless needles and melts at 265 – 266° . The *carbinol*, $\text{C}_{15}\text{H}_{14}\text{O}_3\text{N}_3\text{Cl}$, crystallises in glistening, golden leaflets, melts at 188° , and on prolonged boiling with alcoholic potassium hydroxide yields benzoic acid and *p*-chloronitrodimethyl-*o*-phenylenediamine.

Huebner's nitrophenylbenziminazole (Abstr., 1881, 1131) is 6-nitro-2-phenylbenziminazole, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \left\langle \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} \right\rangle \text{CPh}$, as on methylation it yields a quaternary iodide, $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_3\text{I}$, which crystallises in stellate groups of needles, melts at 249° , and when boiled with alcoholic potassium hydroxide is converted into 6-nitro-2-phenyl-1:3-dimethylbenziminazolol, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \left\langle \begin{smallmatrix} \text{NMe} \\ \text{NMe} \end{smallmatrix} \right\rangle \text{CPh} \cdot \text{OH}$; this crystallises in golden leaflets, melts at 192° , and on hydrolysis yields benzoic acid and *m*-nitrodimethyl-*o*-phenylenediamine.

2-*o*-Nitrophenyl-1:3-dimethylbenziminazolium iodide, $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_3\text{I}$, prepared from 2-*o*-nitrophenylbenziminazole, crystallising in colourless prisms (brown leaflets: Walther and Pulawski, Abstr., 1899, i, 639), crystallises in red, dichroic octahedra, forms a yellow powder when pulverised, melts above 280° , and when warmed with aqueous potassium hydroxide forms the *carbinol*. This crystallises in large,

orange prisms, melts at 210° , and yields only traces of *s*-dimethyl-*o*-phenylenediamine on prolonged boiling with alcoholic potassium hydroxide.

2-m-Nitrophenyl-1:3-dimethylbenziminazolium iodide crystallises in flat, yellow needles and melts at high temperatures. *2-m-Nitrophenyl-1:3-dimethylbenziminazolol*, $C_{15}H_{15}O_3N_3$, crystallises in yellow needles, melts at 167° , and is hydrolysed to only a slight extent when boiled with alcoholic potassium hydroxide for several hours.

2-p-Nitrophenylbenziminazole melts at 210° (compare Walther and Pulawski, *loc. cit.*); the quaternary *iodide* formed by heating with methyl iodide crystallises in long, yellow needles, melts above 270° , and when treated with an alkali hydroxide yields *2-p-nitrophenyl-1:3-dimethylbenziminazolol*, which crystallises in yellow prisms and melts at 140° .

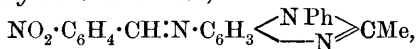
The yellow quaternary iodides described above form colourless aqueous solutions. G. Y.

Some Benziminazoles from 4:2-Nitroaminodiphenylamine. REINHOLD VON WALTHER and ALEX. KESSLER (*J. pr. Chem.*, 1906, [ii], 74, 188—206, 241—248. Compare Abstr., 1904, i, 348).—The *hydrochloride* of 5-nitro-1-phenyl-2-methylbenziminazole crystallises in glistening leaflets and melts at 228° ; the *picrate*,

$C_{14}H_{11}O_2N_3 \cdot C_6H_5O_7N_3$, forms yellow needles and does not melt at 270° ; the *methiodide*, $NO_2 \cdot C_6H_3 \left\langle \begin{smallmatrix} NPh \\ N(MeI) \end{smallmatrix} \right\rangle CMe$, crystallises in yellow prisms and commences to decompose at 270° . *5-Nitro-1-phenyl-2:3-dimethylbenziminazolol*, $NO_2 \cdot C_6H_3 \left\langle \begin{smallmatrix} NPh \\ NMe \end{smallmatrix} \right\rangle CMe \cdot OH$, prepared by heating the methiodide with aqueous sodium hydroxide, crystallises from benzene in yellow needles, melts at 206° , and is not hydrolysed by boiling alcoholic potassium hydroxide.

5-Amino-1-phenyl-2-methylbenziminazole, $NH_2 \cdot C_6H_3 \left\langle \begin{smallmatrix} NPh \\ N \end{smallmatrix} \right\rangle CMe$, prepared by reduction of the 5-nitro-compound by means of alcoholic ammonium sulphide at 120° under pressure, crystallises from a mixture of ethyl acetate and light petroleum in yellowish-brown needles, melts at 145 — 147° , and is a strong base dissolving readily in dilute acids. The *picrate*, $C_{14}H_{13}N_3 \cdot C_6H_5O_7N_3$, melts at 195° ; the *platinichloride* forms yellow needles and is unstable. The *acetyl* derivative, $NHAc \cdot C_7N_2H_3PhMe$, crystallises in white needles and melts at 229 — 230° . The *benzeneazo*-derivative, $NPh:N \cdot NH \cdot C_7N_2H_3PhMe$, formed by adding a freshly-prepared solution of diazobenzene chloride and sodium acetate to the amine in cooled hydrochloric acid solution, crystallises in yellowish-red needles, melts at 184 — 185° , is insoluble in aqueous sodium hydroxide, evolves nitrogen when heated with hydrochloric acid, and decomposes on prolonged heating with alcohol.

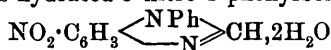
The *p-nitrobenzylidene* derivative,



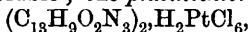
formed by boiling the amine with *p*-nitrobenzaldehyde in alcoholic solution in a reflux apparatus, crystallises in yellow needles and melts at 240°. The *o*-nitrobenzylidene derivative, $C_{21}H_{16}O_2N_4$, crystallises from alcohol in green needles and melts at 153—155°.

When heated with resorcinol at 175°, 5-amino-1-phenyl-2-methylbenziminazole forms an *additive* compound, $C_{14}H_{13}N_3 \cdot C_6H_4(OH)_2$, which crystallises from dilute alcohol in silver-grey needles and melts at 197°. The *thiocarbamide*, $CS(NH \cdot C_7H_5N_2PhMe)_2$, prepared by heating the amine with carbon disulphide and a small quantity of flowers of sulphur in alcoholic solution in a sealed tube at 100°, crystallises from dilute alcohol in white needles, sinters at 130°, and melts and decomposes at 141°. 5-Phenylcarbamido-1-phenyl-2-methylbenziminazole, $NHPh \cdot CO \cdot NH \cdot C_7H_5N_2PhMe$, formed by the action of phenylcarbimide on the amine in ethereal solution, crystallises from alcohol and melts and decomposes at 140—143°.

4-Nitro-2-formylaminodiphenylamine, $CHO \cdot NH \cdot C_6H_4(NO_2) \cdot NHPh$, prepared by the action of anhydrous formic acid on 4-nitro-2-aminodiphenylamine at the ordinary temperature, crystallises from alcohol in golden needles, melts at 182°, and gives a characteristic deep violet coloration with concentrated sulphuric acid. When heated with 40 per cent. sulphuric acid on the water-bath, 4-nitro-2-formylamino-diphenylamine yields hydrated 5-nitro-1-phenylbenziminazole,

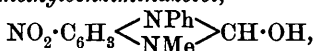


(compare Reissert and Goll, *Abstr.*, 1905, i, 247), which crystallises in colourless needles and melts at 134°; the anhydrous benziminazole obtained by heating the hydrated substance on the water-bath, or recrystallising it from alcohol, or by heating 4-nitro-2-aminodiphenylamine with an excess of ethyl-*o*-formate in a reflux apparatus on the water-bath, or by heating 4-nitro-2-formylaminodiphenylamine with hydrochloric acid, crystallises in colourless needles and melts at 156°. The *nitrate*, $C_{13}H_9O_2N_3 \cdot HNO_3$, crystallises in white needles, melts at 205°, and is sparingly soluble; the *platinichloride*,



forms yellow needles; the *methiodide*, $NO_2 \cdot C_6H_3 \begin{array}{c} \text{NPh} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{CH}_3$, crystallises in stout, yellow needles and commences to melt and decompose at 245°.

5-Nitro-1-phenyl-3-methylbenziminazolol,



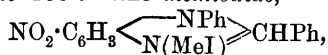
obtained by treating the methiodide with sodium hydroxide in cooled aqueous solution, crystallises in yellow needles and melts at 200°. When heated with alcoholic potassium hydroxide, the methiodide is hydrolysed, forming 4-nitro-2-methylaminodiphenylamine,



which crystallises from alcohol, is yellow, and melts at 155—156°. It is converted by boiling with acetic anhydride in glacial acetic solution into 5-nitro-1-phenyl-2 : 3-dimethylbenziminazolol, melting at 206°.

When heated with concentrated hydrochloric acid at 150°, 4-nitro-2-benzoylamino-diphenylamine, prepared by boiling 4-nitro-2-aminodi-

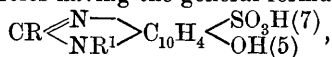
phenylamine with benzoic anhydride in alcoholic solution (compare Muttelet, Abstr., 1898, i, 412), is converted into the insoluble *hydrochloride* of 5-nitro-1 : 2-diphenylbenziminazole, $C_{19}H_{13}O_2N_3 \cdot HCl$, which crystallises in silvery needles melting at 236° ; the base melting at 181 — 182° is formed when 4-nitro-2-benzoylamino-diphenylamine is heated with dilute sulphuric acid at 100° and treated with concentrated sulphuric acid, or when 4-nitro-2-aminodiphenylamine is heated with benzoic anhydride at 180° . The *methiodide*,



crystallises from methyl alcohol in yellow needles, commences to melt and decompose at 260° , and when treated with potassium hydroxide in hot methyl-alcoholic solution yields the yellow carbinol (?) melting at 190° , and, on further heating, 4-nitro-2-aminodiphenylamine.

5-Amino-1 : 2-diphenylbenziminazole, prepared by reduction of the 5-nitro-base with zinc dust and alcoholic hydrogen chloride, forms an *acetyl* derivative, $NHAc \cdot C_6H_3 \begin{array}{c} \text{NPh} \\ \text{N} \end{array} \text{CPh}$, which crystallises in glistening needles and melts at 254° . G. Y.

[**Hydroxynaphthiminazoles and their Azo-derivatives.**] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 172319).—The hydroxynaphthiminazoles having the general formula



where R and R^1 are either hydrogen atoms or aliphatic or aromatic groups, are produced by the action of aldehydes or mixtures in molecular proportion of aldehydes and ketones, or of acid anhydrides or chlorides, on 5-hydroxy-1 : 2-naphthylenediamine-7-sulphonic acid. When acid anhydrides or chlorides are employed, the acyl derivative first obtained is heated with acids, when the iminazole ring is formed.

μ -Methyl-1 : 2-naphthiminazole-5-hydroxy-7-sulphonic acid is prepared by treating a neutral solution of 5-hydroxy-1 : 2-naphthylenediamine-7-sulphonic acid with acetic anhydride. When the solution no longer gives a coloration with sodium nitrite, it is heated to boiling and finally cooled, when the new compound crystallises out. By replacing acetic anhydride by benzoyl or *p*-nitrobenzoyl chloride in the foregoing condensation, 5-hydroxy- *μ -phenyl-1 : 2-naphthiminazole-7-sulphonic acid* and the corresponding *p-nitrophenyl* derivative are produced.

Phthalic anhydride may likewise be employed when *μ -carboxyphenyl-1 : 2-naphthiminazole-5-hydroxy-7-sulphonic acid* is formed.

G. T. M.

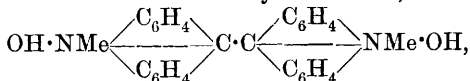
Molecular Weight of Indigotin. ERNST BECKMANN and WERNER GABEL (*Ber.*, 1906, 39, 2611—2618).—The authors have extended the experiments of Vaubel (Abstr., 1901, i, 714; 1902, i, 542) on the molecular weight of indigotin. Whilst Vaubel found, by the cryoscopic method with phenol and *p*-toluidine respectively, a molecular weight for indigotin corresponding with twice the value demanded by the Baeyer formula, the ebullioscopic determinations now quoted by the authors gave values corresponding with the single formula. The solvents used were quinoline, aniline, phenol, and *p*-toluidine.

The molecular rises of the boiling point of phenol and *p*-toluidine respectively were redetermined and found to be 34.40° and 41.40° .

Cryoscopic measurements with aniline and with phenol gave values corresponding with the single formula. Whilst the authors' results with phenol are at variance with Vaubel's, the results with *p*-toluidine agree. A. McK.

Molecular Weight of Indigotin. HERMANN WICHELHAUS (*Ber.*, 1906, 39, 3298. Compare Beckmann and Gabel, preceding abstract).—The author draws attention to his determination of the molecular weight of α -naphthaleneindigo (*Abstr.*, 1894, i, 42). G. Y.

Reduction of Cyclic Amine-ones. I. Preparation of Acridine from Acridone. HERMAN DECKER and GEORGES DUNANT (*Ber.*, 1906, 39, 2720—2722).—When reduced with zinc and acetic acid, 10-methylacridone yields a mixture of a diacridyl derivative,



methylacridonium hydroxide, and methyl dihydroacridine. The last is readily oxidised by 2 per cent. nitric acid to a methylacridonium nitrate.

As the acridonium salts are readily converted into acridine and methyl esters, these processes afford a convenient method for transforming acridone into acridine. J. J. S.

Action of Imino-ethers on Amino-esters. HERMANN FINGER and L. SCHUPP (*J. pr. Chem.*, 1906, [ii], 74, 154).—4-Keto-2-phenyl-1:4-dihydroquinazoline, melting at 241° , is formed when a molecular mixture of benziminoethyl ether and methyl anthranilate is heated.

Imino-ethers condense in the same manner with α - and β -amino-esters of the fatty series. G. Y.

Diacridines. CARLO BAEZNER [in part with J. GUEORGUEFF and AUGUST GARDIOL] (*Ber.*, 1906, 39, 2650—2653. Compare this vol., i, 699, 887).—In the preparation of hydroxynaphthacridines by the reduction of *o*-nitrobenzyl chlorides with stannous chloride in the presence of dihydroxynaphthalenes, substances were obtained as by-products which were insoluble in alkali. These products became the main products of the action when the nitro-compound was used in the proportion of 2 mols. to 1 mol. of naphthol.

3':3''-Diamino-2:7-naphthalenediacridine, $\text{C}_{24}\text{H}_{16}\text{N}_4$, is obtained from *o*-*p*-dinitrobenzyl chloride and 2:7-dihydroxynaphthalene, whilst 3'-amino-7-hydroxy-1:2-phenonaphthacridine is also obtained. The former separates from nitrobenzene in yellowish-red needles and decomposes at 360° . Its salts with mineral acids are highly coloured. Its diacetyl derivative separates from nitrobenzene in yellow needles and melts at 240 — 245° .

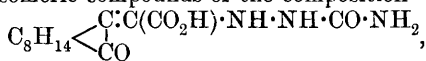
3':3''-Diamino-2:3-naphthalenediacridine, $\text{C}_{24}\text{H}_{16}\text{O}_4$, obtained from *o*-*p*-dinitrobenzyl chloride and 2:3-dihydroxynaphthalene, separates from xylene in greyish-yellow needles. Its solution in concentrated sulphuric acid is yellow and exhibits bluish-green fluorescence. Its

hydrochloride separates from dilute hydrochloric acid in violet-red crystals.

The reduction of *o*-nitrobenzyl chloride in presence of 2 : 7-dihydroxynaphthalene yielded, in addition to 7-hydroxy-1 : 2-phenonaphthacridine, a product insoluble in alkali but partly soluble in xylene. From the xylene solution a compound $C_{24}H_{18}ON_2$ was isolated; it melted at 123—125°.

A. McK.

Action of Amines on Camphoroxalic Acid. J. BISHOP TINGLE and CHARLES J. ROBINSON (*Amer. Chem. J.*, 1906, **36**, 223—290).—By the action of semicarbazide on camphoroxalic acid, J. B. and A. Tingle (*Abstr.*, 1900, i, 302) obtained a product which seemed to consist of two isomeric compounds of the composition



which melted at 218° and 209—210° respectively. Tingle and Hoffman (*Abstr.*, 1905, i, 800) obtained a similar compound which they termed semicarbazidocamphoformeneaminecarboxylic acid, which on crystallisation from alcohol melted at 200°, but when crystallised from glacial acetic acid melted at 209—210°. These experiments have been repeated and the apparently isomeric substances have been proved to be identical, the differences observed in the melting point being due to differences in the rate of heating. When camphoroxalic acid is heated with semicarbazide at 125° under pressure, hydrazodicarbamide and camphylpyrazolecarboxylic acid are obtained. The same compounds, together with camphyl-3-keto-1 : 2 : 4-heptatriazine, are produced when carbamylcamphoformeneaminecarboxylic acid (semicarbazidocamphoformeneaminecarboxylic acid) is heated at its melting point for twenty minutes.

Camphylpyrazolecarboxylic acid, $C_8H_{14} \begin{array}{c} C \text{---} C \cdot CO_2H \\ \diagup \quad \diagdown \\ C \cdot NH \cdot N \end{array}$, forms stout, colourless, prismatic crystals, melts at 255—258°, and is soluble in alcohol or acetone and slightly so in hot water. On fusion, it is converted into *camphylpyrazole*, $C_8H_{14} \begin{array}{c} C \cdot CH \\ \diagup \quad \diagdown \\ C \cdot NH \end{array} > N$, which remains unmelted at 288°.

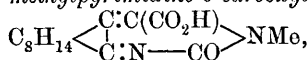
Camphyl-3-keto-1 : 2 : 4-heptatriazine, $C_8H_{14} \begin{array}{c} C \cdot CH \cdot NH \\ \diagup \quad \diagdown \\ C = N \cdot CO \end{array} > NH$, crystallises from alcohol in small, yellow prisms, melts at 305—306°, and is sparingly soluble in ether, acetone, benzene, or light petroleum.

Ethyl carbamylcamphoformeneaminecarboxylate (J. B. Tingle and A. Tingle, *loc. cit.*) melts at 191°, but the melting point varies with the rate of heating. If the ester is left in contact with the alcoholic hydrogen chloride solution in which it was produced, it undergoes decomposition with formation of *ethyl camphylpyrazolecarboxylate*, which crystallises from light petroleum in large, hemimorphic, monoclinic prisms and melts at 91—92°; its *hydrochloride* softens at 151° and melts at 156°.

When an alcoholic solution of camphoroxalic acid and carbamide is

heated under pressure at 135° , *formamidylcamphoformeneaminecarboxylic acid*, $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{C}:\text{C}(\text{CO}_2\text{H})\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 \\ | \\ \text{CO} \end{smallmatrix}$, is produced, which melts and decomposes at $192\text{--}194^{\circ}$ and is readily soluble in alcohol and sparingly so in acetone, ethyl acetate, or chloroform.

Methylcarbamide reacts with camphoroxalic acid with formation of *2-keto-4:5-camphyl-1-methylpyrimidine-6-carboxylic acid*,



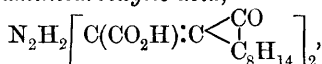
which crystallises in long, pale yellow prisms, melts at 154° , and dissolves readily in ether, acetone, chloroform, or hot alcohol.

By the interaction of *s*-dimethylcarbamide and camphoroxalic acid, a small quantity of a substance melting at $104\text{--}105^{\circ}$ is obtained, together with a larger amount of *methylcamphoformeneaminecarboxylic acid*, $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{C}:\text{C}(\text{CO}_2\text{H})\cdot\text{NHMe} \\ | \\ \text{CO} \end{smallmatrix}$, which crystallises in long, colourless,

prismatic needles, melts at $77\text{--}78^{\circ}$, and is very soluble in the usual organic solvents. Attempts were made to obtain condensation products of camphoroxalic acid and *as*-dimethylcarbamide, but without success.

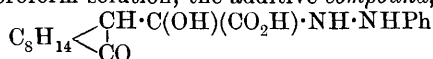
Camphoroxalic acid reacts with a solution of hydrazine in methyl alcohol at the ordinary temperature with formation of hydrazine camphoroxalate, biscamphoformeneaminecarboxylic acid, and camphylpyrazolecarboxylic acid. *Hydrazine camphoroxalate*, $\text{N}_2\text{H}_4\cdot 2\text{C}_{12}\text{H}_{16}\text{O}_4$, is a pale yellow salt which begins to decompose at 186° and is completely melted at 245° .

Biscamphoformeneaminecarboxylic acid,



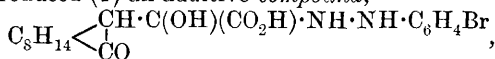
crystallises in long, slender, pale yellow needles with 2 mols. of methyl alcohol, which it loses at 100° and becomes deep yellow; on further heating it begins to decompose at 137° , and is not completely melted at 155° . When the acid is heated at $150\text{--}155^{\circ}$, carbon dioxide is evolved and a product is obtained from which the following three substances were isolated. (1) A compound, $\text{C}_{24}\text{H}_{30}\text{O}_6\text{N}_2$, which crystallises in clusters of pale yellow needles, melts at $222\text{--}223^{\circ}$ and has acid properties. (2) A compound, isomeric with the preceding substance, which has a dull yellow colour and melts at 232° ; solutions of this compound gradually turn red and deposit red crystals which also melt at about 232° . (3) A compound, $\text{C}_{24}\text{H}_{30}\text{O}_5\text{N}_2$, which crystallises in light yellow prisms and melts at 221° .

When phenylhydrazine (2 mols.) is added to camphoroxalic acid (1 mol.) in chloroform solution, the additive compound,



is produced, which crystallises in slender, yellow needles, melts at 120° , and is very stable. If the compound is fused or boiled with alcohol, it is converted into camphylphenylpyrazolecarboxylic acid (Abstr., 1897, i, 484), which melts at 196° and crystallises with 1 mol. of alcohol.

By the action of *p*-bromophenylhydrazine on camphoroxalic acid, there are produced (1) an additive *compound*,



which crystallises in slender, yellow needles, melts at 149° , and is very stable, and (2) a *compound*, $\text{C}_{18}\text{H}_{21}\text{O}_3\text{N}_2\text{Br}$, which melts at 172° . When either of these substances is fused, *camphyl-p-bromophenylpyrazolecarboxylic acid*, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} - \text{C}(\text{CO}_2\text{H}) \\ \diagup \text{C} \cdot \text{N}(\text{C}_6\text{H}_4\text{Br}) \end{array} \text{N}$, is produced which

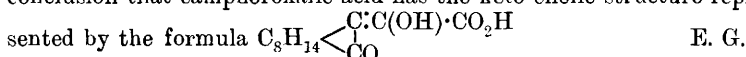
crystallises from benzene in clusters of minute, colourless needles and melts at 215° ; the *ethyl* ester separates from acetone in triclinic crystals, melts at 149° , and, unlike ethyl camphylpyrazolecarboxylate, does not possess basic properties. When this acid is heated at its melting point, carbon dioxide is evolved, and a compound, probably

camphyl-p-bromophenylpyrazole, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} - \text{CH} \\ \diagup \text{C} \cdot \text{N}(\text{C}_6\text{H}_4\text{Br}) \end{array} \text{N}$, is obtained,

which is very soluble in the ordinary organic solvents and, on evaporating its solutions, remains as a gummy mass.

On investigating the hydration product of camphoroxalic acid (Abstr., 1898, i, 443), evidence was obtained that the water is not present as water of crystallisation. The hydration product reacts with aniline and with semicarbazide with formation of substances identical with those obtained from the acid itself. With hydroxylamine, the hydration product yields a *substance* which melts at $181-182^\circ$.

A table is given showing the relations between the various derivatives of camphoroxalic acid which have been obtained by the action of amines, and a summary is made of the various facts which support the conclusion that camphoroxalic acid has the keto-enolic structure represented by the formula



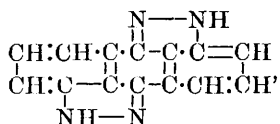
Preparation of Pyrazoles from Anthraquinone Derivatives.

FARBENFABRIKEN VORM. FRIDR. BAYER & Co. (D.R.-P. 171293).—The

pyrazole derivative, $\begin{array}{c} \text{CH} : \text{CH} \cdot \text{C} \cdot \text{CO} - \text{C} - \text{C}(\text{OH}) : \text{CH} \\ \text{CH} : \text{CH} \cdot \text{C} \cdot \text{C} - \text{C} \cdot \text{C} = \text{CH} \\ \text{N} - \text{NH} \end{array}$, is produced by heat-

ing 4-hydrazino-1-hydroxyanthraquinone hydrochloride with aniline and aniline hydrochloride at $170-180^\circ$. At first a molecular compound of the substance with aniline is obtained, but the base is removed on washing with solvents. This pyrazole derivative dissolves in concentrated sulphuric acid or aqueous sodium hydroxide to a yellow solution having an intense green fluorescence.

The *monopyrazole* derivative, $\begin{array}{c} \text{CH} : \text{CH} - \text{C} - \text{C} - \text{C} = \text{CH} \\ \text{CH} : \text{C}(\text{NH} \cdot \text{NH}_2) \cdot \text{C} \cdot \text{CO} - \text{C} \cdot \text{CH} : \text{CH} \\ \text{N} - \text{NH} \end{array}$, is prepared by boiling a slightly acidified aqueous solution of dihydroanthraquinone hydrochloride, when the product separates in graphitic crystals. The *dipyrazole* derivative,



is formed when 1 : 5-disulphohydrazinoanthraquinone is heated at 140° with 3—5 per cent. hydrochloric acid. The product separates as its crystalline hydrochloride, and the base, which, when first set free, is amorphous, gradually assumes a crystalline form and is soluble in dilute aqueous sodium hydroxide to a yellow solution with a green fluorescence. Its solution in concentrated sulphuric acid is colourless, but has an intense blue fluorescence. G. T. M.

Preparation of Azines of the Anthraquinone Series. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 170562).—The *o*-diamines of the anthraquinone series, when condensed with *o*-diketones, furnish azines having the valuable property of dyeing unmordanted cotton. The azine,

The azine, $\begin{array}{c} \text{CH} : \text{CH} : \text{C} \cdot \text{CO} \cdot \text{C} \cdot \text{CH} : \text{C} \cdot \text{N} : \text{C} \cdot \text{C}_6\text{H}_4 \\ \text{CH} : \text{CH} : \text{C} \cdot \text{CO} \cdot \text{C} \cdot \text{CH} : \text{C} \cdot \text{N} : \text{C} \cdot \text{CH} \end{array} > \text{CH}$, obtained by condensing 2 : 3-diaminoanthraquinone and β -naphthaquinone in boiling glacial acetic acid, separates in needles and in the reducing vat produces yellow shades on cotton. Similar azines were produced from 2 : 3-diaminoanthraquinone with phenanthraquinone, β -anthraquinone, and the oxidation product of alizarin-blue. 1 : 2-Diaminoanthraquinone also gives rise to an azine with β -naphthaquinone, whilst two products are obtained on condensing it with β -anthraquinone. G. T. M.

Constitution of *iso*Rosindone and Allied Substances. HERMAN DECKER and AUGUST WÜRSCH (*Ber.*, 1906, **39**, 2653—2656).—The inactivity of *isorosindone* towards magnesium phenyl bromide is an argument in favour of the phenolbetaine formula. The substance is unimolecular in benzene solution. C. S.

1-Amino-3 : 4-triazole (*N*-Amino- $\beta\beta'$ -pyrrodiazole). A Contribution to the Knowledge of the so-called "*N*-Dihydro-tetrazine" (*iso*Bisdiazomethane, Trimethinetriazoimide). CARL BÜLOW (*Ber.*, 1906, **39**, 2618—2622).—The compound described by Curtius and Lang as trimethinetriazoimide and by Hantzsch and Silberrad as dihydrotetrazine, $\text{CH} \begin{array}{c} \text{NH} \cdot \text{N} \\ \text{N} \cdot \text{NH} \end{array} > \text{CH}$, is considered by the

author to be 1-amino-3 : 4-triazole, $\text{NH}_2 \cdot \text{N} \begin{array}{c} \text{CH} : \text{N} \\ \text{CH} : \text{N} \end{array}$. The behaviour of the compound was not in satisfactory accord with the formulæ advanced by previous authors. The new formula, however, is not contradictory to the fact that the compound yields a monoacetyl derivative only and not a diacetyl one, since it would be expected that the salts formed would undergo hydrolysis. Again, the formula accords with the formation of a 1 : 3 : 4-triazole by the action of nitrous acid. Further, the formation of condensation products with aldehydes is readily accounted for.

A direct proof that the so-called dihydrotetrazine is in reality 1-amino-3:4-triazole is afforded by its comportment with ethyl diacetylsuccinate (compare Bülow, Abstr., 1903, i, 196; Bülow and Sautermeister, Abstr., 1904, i, 690), when the action represented by the following equation takes place:

$$2\text{H}_2\text{O} + \begin{array}{c} \text{N}:\text{CH} \\ | \\ \text{N}:\text{CH} \end{array} > \text{N} \cdot \text{NH}_2 + \begin{array}{c} \text{OH} \cdot \text{CMe}:\text{C} \cdot \text{CO}_2\text{Et} \\ | \\ \text{OH} \cdot \text{CMe}:\text{C} \cdot \text{CO}_2\text{Et} \end{array} =$$

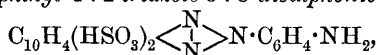
$$\begin{array}{c} \text{N}:\text{CH} \\ | \\ \text{N}:\text{CH} \end{array} > \text{N} \cdot \text{N} < \begin{array}{c} \text{CMe}:\text{C} \cdot \text{CO}_2\text{Et} \\ | \\ \text{CMe}:\text{C} \cdot \text{CO}_2\text{Et} \end{array}$$

Ethyl 1:1-triazole-2:5-dimethylpyrrole-3:4-dicarboxylate, prepared in the manner indicated, crystallises from water in needles and melts at 146—147°.

It follows that Hantzsch and Silberrad's *N*-dihydrotetrazinedicarboxylic acid, $\text{CO}_2\text{H} \cdot \text{C} \begin{array}{c} \text{N} \cdot \text{NH} \\ | \\ \text{NH} \cdot \text{N} \end{array} > \text{C} \cdot \text{CO}_2\text{H}$, is 1-amino-3:4-triazole-2:5-carboxylic acid, $\text{NH}_2 \cdot \text{N} \begin{array}{c} \text{C}(\text{CO}_2\text{H}) \cdot \text{N} \\ | \\ \text{C}(\text{CO}_2\text{H}) \cdot \text{N} \end{array}$.

A. McK.

[*p*-Aminophenylnaphthyl-1:2-triazole-3:8-disulphonic Acid.]
AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 170513).—*p*-Aminophenylnaphthyl-1:2-triazole-3:8-disulphonic acid,



is obtained by successively condensing α -naphthylamine-3:8-sulphonic acid with diazotised *p*-nitroaniline, oxidising the azo-compound thus formed to the corresponding nitrotriazole derivative, and then reducing the nitro-group with acid or alkaline reducing agents.

This aminotriazolesulphonic acid, when diazotised and combined with β -naphthol-3:6-disulphonic acid, furnishes a useful violet, lake-forming azo-derivative.

G. T. M.

Diazobenzene Perchlorate and Phenylacridine Perchlorate
DANIEL VORLÄNDER (*Ber.*, 1906, 39, 2713—2715).—10-Phenylacridine dissolved in dilute 2—3 per cent. sulphuric acid gives with a dilute solution of perchloric acid (1 in 100) a voluminous precipitate of phenylacridine perchlorate consisting of slender, yellow needles. With a more dilute solution (1 in 1000) a turbidity is first produced, and then long, yellow needles separate. Chloric and hypochlorous acids do not yield precipitates except in more concentrated solutions. The test for perchloric acid is not conclusive, since a few acids, nitric acid in particular, form sparingly soluble salts of phenylacridine.

Diazobenzene perchlorate, $\text{C}_6\text{H}_5 \cdot \text{N}_2 \cdot \text{ClO}_4$, separates in white needles when aniline is diazotised in perchloric acid solution, or when a 10 per cent. solution of diazobenzene chloride is treated with perchloric acid. It explodes even in the wet state, but remains white in the cold for one day.

The diazonium perchlorates obtained from *p*-toluidine, *p*-nitroaniline, *o*-, *m*-, and *p*-chloroaniline, *p*-bromoaniline, *o*-, *m*-, and *p*-aminobenzoic acid, *o*- and *p*-anisidine, and benzidine have been prepared. The para-compounds are the least unstable.

C. S.

Diazonium Perchlorates. KARL A. HOFMANN and H. ARNOLDI (*Ber.*, 1906, **39**, 3146—3148).—*Diazobenzene perchlorate*, $C_6H_5 \cdot N_2 \cdot ClO_4$, prepared by diazotising an aqueous solution of aniline in a mixture of hydrochloric and perchloric acids, is sparingly soluble in water and is a very violent explosive. Compounds with similar explosive properties were obtained from *o*-toluidine, *p*-toluidine, α -naphthylamine, and β -naphthylamine respectively
A. McK.

Preparation of Diazo-oxynaphthalenesulphonic Acids and their Anhydrides. ANILINFARBEN- & EXTRACT-FABRIKEN VORM. J. R. GEIGY (D.R.-P. 171024).—The *o*-aminonaphthols and their sulphonic acids are not readily diazotised by the ordinary process, oxidation occurs, and β -naphthaquinone derivatives may be formed. This result occurs to some extent even in the absence of mineral acid, and is increased on warming the solution. It has now been ascertained that the addition of a comparatively small amount of a cupric salt renders the diazotisation of the aminonaphtholsulphonic acid complete even in the absence of mineral acid, and at the same time reduces the oxidising action to a minimum. To a well-cooled thin paste of 1-amino- β -naphthol-4-sulphonic acid were added successively cold concentrated solutions of copper sulphate and sodium nitrite. The diazotisation proceeded quite smoothly, the product being soluble and yielding an orange-yellow solution from which 1-diazo-2-oxynaphthalene-4-sulphonic acid, $HSO_3 \cdot C_{10}H_6 \cdot \begin{smallmatrix} N \\ \diagup \diagdown \\ O \end{smallmatrix}^2$, separated in fine yellow needles on the addition of concentrated hydrochloric acid. This diazo-compound, which is not explosive when dry, combines with resorcinol to furnish a dark violet azo-derivative.

Barium-1-diazo-2-oxynaphthalene-6-sulphonate was obtained as a golden-yellow, crystalline precipitate on adding successively copper chloride, sodium nitrite, hydrochloric acid, and barium chloride to a cold aqueous solution of 1-amino- β -naphthol-6-sulphonic acid. *Barium-1-diazo-2-oxynaphthalene-7-sulphonate*, a light brown, crystalline substance, was prepared in a similar manner.

1-Diazo-2-oxynaphthalene-8-sulphonic acid, produced from the corresponding 1-amino- β -naphthol-8-sulphonic acid, separates in colourless needles with a silvery lustre; this substance condenses with the phenols only with some difficulty; in the case of alkaline resorcinol, the solution has to be strongly heated.

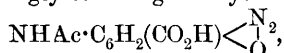
The diazo-oxides of the 1-amino- β -naphtholdisulphonic acids were also prepared through the agency of a cupric salt, and were isolated either as alkali or barium salts, and 1-diazo-2-oxynaphthalene-3 : 6 : 8-trisulphonic acid was obtained in the form of its crystalline, orange-yellow acid sodium salt.

In some cases a ferrous salt was employed instead of the copper compound. The mono-, di-, and tri-sulphonic acids of 2-amino- α -naphthol were also diazotised in this way, and were usually isolated in the form of the crystalline, yellow sodium salts. The patent contains a tabulated description of seventeen new diazo-oxynaphthalene sulphonic acids.
G. T. M.

Preparation of the Anhydrides of 1-Diazo-2-hydroxy- and 2-Diazo-1-hydroxy-naphthalenes. ANILINFARBEN- & EXTRACT-FABRIKEN VORM. J. R. GEIGY (D.R.-P. 172446. Compare preceding abstract).—1-Amino- β -naphthol and 2-amino- α -naphthol can both be readily diazotised by treating the aqueous solutions of their hydrochlorides with a dilute solution of sodium nitrite and copper sulphate.

1-Diazo-2-oxynaphthalene, $C_{10}H_6\langle\overset{N}{\underset{O}{|}}\rangle^2$, is precipitated in yellow crystals on the addition of sodium chloride, whilst the crude 2-diazo-1-oxynaphthalene separates in yellowish-green crystals which are re-dissolved in the solution at 86° , and reprecipitated in yellow crystals on cooling. These compounds are very sensitive to light, darkening rapidly even in diffused daylight. G. T. M.

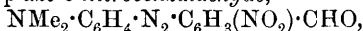
Azo-derivatives of 3-Amino-5-acetylaminosalicylic Acid. LEOPOLD CASSELLA & Co. (D.R.-P. 170819).—3-Amino-5-acetylaminosalicylic acid, $OH\cdot C_6H_2(NH_2)(NHAc)\cdot CO_2H$, which is obtained by successively nitrating and reducing acetyl-*p*-aminosalicylic acid, yields on diazotisation a sparingly soluble golden-yellow diazo-derivative,



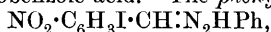
which combines with the sulphonic acids of the naphthols and dihydroxynaphthalenes to furnish a series of valuable mordant dyeing colouring matters. G. T. M.

***para*-Substituted *o*-Nitrobenzaldehydes.** V. FRANZ SACHS and HERMANN KANTOROWICZ (*Ber.*, 1906, 39, 2754—2762. Compare Abstr., 1902, i, 377, 682; 1903, i, 425; 1904, i, 62, 506, 593; 1905, i, 202; this vol., i, 575).—2-Nitrobenzaldehyde-4-diazonium sulphate, $CHO\cdot C_6H_3(NO_2)\cdot N_2\cdot SO_4H$, obtained by the action of amyl nitrite and sulphuric acid on 2-nitro-4-aminobenzaldoxime, is a pale yellow solid, readily soluble in water, but insoluble in most organic solvents, and decomposes when exposed to the air. The corresponding chloride, $C_7H_4O_3N_3Cl$, is more explosive and also more reactive.

Dimethylaniline-p-azo-o-nitrobenzaldehyde,



obtained by coupling the chloride with an acetic acid solution of dimethylaniline, crystallises in bordeaux-red, glistening plates and melts at 219 — 220° . It dissolves readily in most organic solvents, but only sparingly in water, and readily dyes silk or wool. The *phenylhydrazine* gives a deeper shade of colour and is faster. *Naphthol-p-azo-o-nitrobenzaldehyde*, $OH\cdot C_{10}H_6\cdot N_2\cdot C_6H_3(NO_2)\cdot CHO$, crystallises from acetic acid, melts at 208° , and is only sparingly soluble in water. *Phenol-p-azo-o-nitrobenzaldehyde*, $OH\cdot C_6H_4\cdot N_2\cdot C_6H_3(NO_2)\cdot CHO$, melts at 162° , dyes wool or silk rose-red, and yields a *phenylhydrazone*. 4-Iodo-2-nitrobenzaldehyde, $NO_2\cdot C_6H_3I\cdot CHO$, melts at 112° and resembles the corresponding chloro- and bromo-compounds, but is far less stable, and, after exposure to sunlight for several hours is transformed into iodonitrosobenzoic acid. The *phenylhydrazone*,



crystallises from alcohol in red needles melting at 185° , and the *semicarbazone*, $C_8H_7O_3N_4I$, from acetic acid in pale yellow, rectangular plates, which melt and decompose at 284° .

2-Nitro-4-hydroxybenzaldehyde, $NO_2 \cdot C_6H_3(OH) \cdot CHO$, obtained by decomposing the diazonium salts, crystallises from alcohol in yellow needles melting at 67° and has an intense odour. The *phenylhydrazone*, $C_{13}H_{11}O_3N_3$, forms glistening, red needles and melts at $189-190^{\circ}$.

2:4-Dinitrobenzaldehyde-p-bromophenylhydrazone forms red crystals melting at $226-227^{\circ}$, and its alcoholic solution gives a characteristic blue colour on the addition of a drop of potassium hydroxide solution. The corresponding *phenylmethylhydrazone*, $C_{14}H_{12}O_4N_4$, forms purple-red crystals melting at 194° .

2:4:6-Trinitrobenzaldehyde-p-bromophenylhydrazone, $C_{13}H_8O_6N_5Br$, crystallises from acetic acid in glistening, reddish-brown prisms melting at 242° . *Trinitrobenzaldehydephenylhydrazone-p-sulphonic acid*,

$C_6H_2(NO_2)_3 \cdot CH:N_2H \cdot C_6H_4 \cdot SO_3H$, crystallises in pale red needles melting at 211° . It dissolves in alcohol and also in hot water, the aqueous solution giving brilliant but unstable colours with potassium hydroxide. Trinitrobenzaldehyde combines with sodium hydrogen sulphite and also yields a *semicarbazone*, $C_8H_6O_7N_6$, in the form of pale yellow plates melting at 214° . *Trinitrobenzylidenebenzidine*, $C_6H_2(NO_2)_3 \cdot CH:N \cdot C_{12}H_8 \cdot NH_2$, crystallises from xylene or amyl alcohol in glistening, blood-red plates melting at 223° and readily soluble in acetone or nitrobenzene. *Trinitrobenzylideneaniline*, $C_{13}H_8O_6N_4$, crystallises in reddish-yellow needles melting at 162° .

When reduced with alcoholic ammonium sulphide, the trinitroaldehyde yields an extremely unstable pale yellow compound.

2:6-Dinitro-4-aminobenzaldehydephenylhydrazone, $C_{13}H_{11}O_4N_5$, obtained by the action of phenylhydrazine on the oxime, melts at 250° .

2:6-Dinitrobenzaldehyde-4-diazonium chloride, $C_7H_3O_5N_4Cl$, is readily soluble in water, and explodes violently when heated. The azo-derivatives of *o*-nitrobenzaldehyde do not yield indigo dyes with acetone and alkali.

J. J. S.

Azo-colouring Matters of the Pyridine Series. R. BAUMERT (*Ber.*, 1906, 39, 2971—2976).—Azo-colouring matters containing the pyridine ring have not hitherto been obtained, but by diazotising *p*-amino-4-stilbazole and *p*-amino-2-stilbazole, and coupling the products with phenols and amines, compounds of this kind have now been obtained.

p-Nitro-4-stilbazole, $C_6NH_4 \cdot CH:CH \cdot C_6H_4 \cdot NO_2$, prepared by heating approximately equal weights of γ -picoline, *p*-nitrobenzaldehyde, and freshly melted zinc chloride for nine hours at $150-160^{\circ}$, was obtained in the form of brown crusts after removing unaltered γ -picoline by distillation in steam; it forms yellow needles melting at $118-119^{\circ}$, is almost insoluble in water, and dissolves readily in organic media. Its crystalline *hydrochloride* melts at $257-258^{\circ}$; the *platini*- and *aurochlorides* are also crystalline.

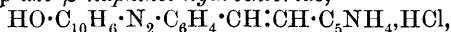
p-Amino-2-stilbazole, obtained by reducing *p*-nitro-2-stilbazole, crystallises from dilute alcohol in pale yellow needles melting at $138-139^{\circ}$;

its *stannochloride*, $C_{13}H_{14}N_2Cl_2 \cdot 2SnCl_2$, obtained during the reduction, melts at 198—199°; the *platinichloride* forms yellow needles.

Di-2-stilbazylthiocarbamide, $C_{27}H_{22}N_4S$, which results from the condensation of *p*-amino-2-stilbazole and carbon disulphide in alcoholic potash, melts at 180—181° and forms a yellow *platinichloride*, $C_{27}H_{22}N_4S(H_2PtCl_6)_2$. *Acetyl-p-amino-2-stilbazole*, $C_{15}H_{14}ON_2$, crystallises from dilute alcohol in slender needles and melts at 170—171°.

p-Amino-4-stilbazole, prepared by reducing *p*-nitro-4-stilbazole, melts at 138—139°; its *hydrochloride* and *stannochloride*, $C_{13}H_{14}N_2Cl_2 \cdot 2SnCl_2$, melt at 257—258° and 198—199° respectively; the *platinichloride* melts above 300°. The *thiocarbamide* derivative melts at 195—196°; its *platinichloride* melts above 300°.

2-Stilbazole-p-azo-β-naphthol hydrochloride,

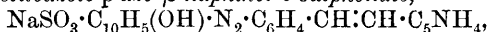


was obtained by adding a solution of diazotised *p*-amino-2-stilbazole to alkaline β-naphthol and subsequently acidifying the solution of the azo-compound. This salt, which crystallises from 90 per cent. alcohol in reddish-brown leaflets, melts at 252—253° and dyes silk, wool, and ordinary and mordanted cotton; it is only slightly soluble in water, and, like benzeneazo-β-naphthol, is devoid of phenolic properties, being insoluble in aqueous alkali hydroxides.

4-Stilbazole-p-azo-β-naphthol hydrochloride resembles its isomeride, but dyes in somewhat deeper shades and melts at 257—258°.

The hydrochlorides of *2-stilbazole-p-azoresorcinol* and *4-stilbazole-p-azoresorcinol* are brown powders sparingly soluble in water, more so in alcohol, and dissolving in aqueous alkali hydroxides.

Sodium 2-stilbazole-p-azo-β-naphthol-6-sulphonate,



crystallises from 90 per cent. alcohol in needles having a green, metallic lustre; its isomeride from diazo-4-stilbazole has similar properties. Similar dyes can be obtained from the two isomeric diazostilbazoles with β-naphthol-3 : 6-disulphonic acid and also with β-naphthol-6 : 8-disulphonic acid, salicylic acid, dimethylaniline, and sulphanilic acid.

G. T. M.

Tertiary Aromatic Amines. V. CARL HAEUSSERMANN (*Ber.*, 1906, 39, 2762—2765).—*Tetraphenyldiaminoazobenzene*, $C_{36}H_{28}N_4$, is obtained when nitrotriphenylamine is reduced electrolytically. The best results are obtained when the cathode compartment contains an alcoholic solution of the nitro-compound and sodium acetate, the anode compartment an aqueous solution of sodium hydroxide, and the electrodes are of nickel gauze or platinum.

The azo-compound separates from benzene as orange-red crystals melting at 201—202·5°, and is only sparingly soluble in alcohol or acetone.

Aminotriphenylamine (Herz, *Abstr.*, 1890, 1409), obtained by the action of ammonia on its hydrochloride, crystallises from ether or alcohol in glistening, colourless needles melting at 146—147·5° and distilling above 360°.

Triphenylamine does not readily condense with diazobenzene chloride, whereas diphenyl-*m*-toluidine reacts with an acetic acid

solution of diazobenzene chloride, yielding *benzeneazodiphenyl-m-toluidine*, $C_{25}H_{21}N_3$, which, after repeated crystallisation from acetone, forms scarlet-red needles melting at 168—169°. It is readily soluble in benzene, but less so in alcohol.

Triphenylamine and benzaldehyde condense in the presence of 50 per cent. sulphuric acid, yielding a pale green product which, after extraction with alcohol, is colourless. It probably consists of tetraphenyldiaminotriphenylmethane. J. J. S.

Azimino-compounds from Aromatic *para*-Diamines.

GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT (*Ber.*, 1906, 39, 2869—2875. Compare *Trans.*, 1905, 87, 73; 1906, 89, 1158).—*p*-Toluenesulphonyl-5-nitro-*o*-toluidine (Reverdin and Crépieux, *Abstr.*, 1902, i, 238, 434) may be obtained by the action of *p*-toluenesulphonic chloride on a boiling toluene solution of 5-nitro-*o*-toluidine; when reduced with iron filings and dilute acetic acid, it yields *p*-toluenesulphonyl-*p*-toluenyldiamine, $NH_2 \cdot C_6H_3Me \cdot NH \cdot SO_2 \cdot C_7H_7$
 $[NH_2 : Me : NH = 1 : 3 : 4]$,

which crystallises from dilute alcohol in slender prisms melting at 150°. When the diazonium chloride derived from the base is mixed with excess of sodium acetate solution, it yields *p*-toluenesulphonyl-*p*-aziminotoluene, $C_6H_3Me \cdot \begin{smallmatrix} N \cdot SO_2 \cdot C_7H_7 \\ | \\ N_2 \end{smallmatrix}$; this is practically insoluble in

the usual organic solvents, but dissolves sparingly in hot pyridine, naphthalene, or *p*-toluidine. It has a pale yellow colour and decomposes violently at 156°. The azimino-compound is converted back into the diazonium salt by cold concentrated hydrochloric acid and then condenses with β -naphthol, yielding 2-*p*-toluenesulphonylaminotoluene-5-azo- β -naphthol, $OH \cdot C_{10}H_6 \cdot N_2 \cdot C_6H_3Me \cdot NH \cdot SO_2 \cdot C_7H_7$, which crystallises from benzene or acetic acid in glistening, red needles melting at 194°.

The same azo-compound can be obtained by heating equivalent quantities of the azimino-compound and β -naphthol in dry pyridine.

p-Toluenesulphonylmethyl-5-nitro-*o*-toluidine,



obtained by heating Reverdin and Crépieux's nitro-compound with methyl iodide and alkali in methyl-alcoholic solution, melts at 103—105°. When reduced it yields *p*-toluenesulphonylmethyl-*p*-toluenediamine, $NH_2 \cdot C_6H_3Me \cdot NMe \cdot SO_2 \cdot C_7H_7$, which crystallises in colourless plates melting at 118—119°; the corresponding diazonium salt does not yield an azimino-compound with sodium acetate, but couples with β -naphthol to an *azo-dye*, $C_{25}H_{23}O_3N_3S$, which separates from acetic acid in deep red, nodular crystals melting at 181°. J. J. S.

Condensation of Diazobenzeneimides with Pyrazolones.

REINHOLD VON WALTHER and P. ROTHACKER (*J. pr. Chem.*, 1906, [ii], 74, 207—208. Compare Dimroth, *Abstr.*, 1902, i, 403).—The action of various diazobenzeneimides on phenylmethylpyrazolone in presence of sodium ethoxide leads to the formation of a red *product*, which is formed also in small quantities by the interaction of 4-dichloropyrazolone, pyrazolone, and hydrazine. It melts at 184°, is insoluble

in water, only sparingly so in organic solvents, is readily soluble in hot dilute alkali hydroxides or concentrated sulphuric or hydrochloric acid, and forms two series of salts, of which the acid series is yellowish- to blood-red, whilst the normal salts are yellow, and are readily soluble in water, alcohol, or ether; the *platinichloride* can be extracted from its aqueous solution by shaking with ether. The *acetyl* derivative is yellow to dark red, the diacetyl derivative is yellow. The decomposition of the product melting at 184° leads to the formation on the one hand of rubazonic acid and bispyrazolone, and on the other of hydrazine; it contains probably 2 mols. of the pyrazolone coupled by means of a hydrazine group.

1-Phenyl-3:4-dimethylpyrazolone does not react with diazobenzene-imide. G. Y.

Production of Colloidal Preparations containing Gold, Silver, or Copper. KALLE & Co. (D.R.-P. 170433, 170434).—Colloidal substances containing silver or gold are obtained by adding silver nitrate or gold chloride to an alkaline solution of the alkali salts of the fission products of albumin (lysalbumins, protoalbumins, alkali albumoses, &c.), warming gently for some time, and then dialysing the solution. The colloidal solution thus obtained yields a precipitate with dilute acid which may be again dissolved in alkali and purified by repeated dialysis.

An alkaline solution containing sodium protoalbuminate, sodium hydroxide, and copper sulphate, when dialysed until the diffusate was neutral and then evaporated on the water-bath, furnished a brownish-black powder containing 18—19 per cent. of copper, which dissolves in water and aqueous sodium hydroxide to brown and violet solutions respectively. The other fission products of albumin gave rise to similar copper compounds. G. T. M.

Equilibrium between Proteids and Electrolytes. III. Solubility of Globulin in Magnesium Sulphate: Influence of Temperature. GINO GALEOTTI (*Zeit. physiol. Chem.*, 1906, 48, 473—480. Compare Abstr., 1905, ii, 512).—The more concentrated a solution of magnesium sulphate is, the more serum-globulin does it dissolve. When the concentration approaches saturation, the globulin is precipitated, and this precipitation depends on the concentration. The term fractional globulin precipitation should not be used if that expression means that the globulins in the fractions are distinct substances. An increase of temperature increases the solubility of the globulin in dilute solutions of the salt, but lessens it in concentrated solutions. W. D. H.

Hydrolysis of Vitellin. EMIL ABDERHALDEN and ANDREW HUNTER (*Zeit. physiol. Chem.*, 1906, 48, 505—512).—The following figures relate to the monoamino-acids of vitellin from egg yolk, compared with those similarly obtained by hydrolysis from the closely related proteid caseinogen of cow's milk. The numbers given are percentages.

	Vitellin.	Caseinogen.
Glycine	1.1	0
Alanine	present	0.9
Aminovaleric acid	2.4	1.0
Leucine	11.0	10.5
Aspartic acid	0.5	1.2
Glutamic acid	12.2	11.0
Phenylalanine	2.8	3.2
Proline	3.3	3.1
Serine	—	0.23
Tyrosine	1.6	4.5

W. D. H.

Cleavage Products of Vitellin. PHOEBUS A. LEVENE and C. L. ALSBERG (*J. Biol. Chem.*, 1906, 2, 127—133).—One hundred grams of vitellin yield, glycine, traces; alanine, 0.16; leucine, 3.3; proline, 4; aspartic acid, 0.6; glutamic acid, 1; phenylalanine, 1; tyrosine, 0.4; histidine, traces; arginine, 1.2; and lysine, 2.4. The high proportion of proline [pyrrolidine-2-carboxylic acid] is significant in view of the fact that vitellin furnishes the material for the production of hæmoglobin.

W. D. H.

Deaminocasein. ZDENKO H. SKRAUP and PH. HOERNES (*Monatsh.*, 1906, 27, 631—652. Compare Paal, *Abstr.*, 1896, i, 455; Schiff, *ibid.*, 632; Schroetter, *Abstr.*, 1898, i, 610).—The action of sodium nitrite on casein dissolved in glacial acetic acid at the ordinary temperature and finally on the water-bath leads to the formation of *deaminocasein*, $C_{216}H_{349}O_{78}N_{54}SP_{0.4}$; it is obtained as a light yellowish-brown substance, does not give Millon's or the biuret reaction, is much less soluble than is casein in aqueous alkali hydroxides or acids, gives Liebermann's nitroso-reaction, and forms a brown, gelatinous *sodium* derivative. When hydrolysed with boiling 36 per cent. sulphuric acid it yields oxalic acid; the product of the hydrolysis with fuming hydrochloric acid, when treated according to Fischer's method (*Abstr.*, 1901, i, 780), is found to contain leucine, aminovaleric acid, pyrrolidine-2-carboxylic acid, and probably glycine and *isoleucine*; glutamic, caseic, and caseanic acids are present in about the same amounts as, but arginine in much smaller quantity than, in the hydrolysis products of casein. Lysine and tyrosine are not present, whilst the presence of alanine is doubtful.

When boiled with dilute sulphuric acid, casein yields 1.38, deaminocasin 1.77 per cent. of ammonia.

G. Y.

Deaminoglutin. ZDENKO H. SKRAUP (*Monatsh.*, 1906, 27, 653—662. Compare Skraup and Hoernes, preceding abstract).—*Deaminoglutin*, $C_{1039}H_{1669}O_{391}N_{297}S$ or, omitting consideration of the sulphur, $C_{3.51}H_{5.71}O_{1.32}N$ (glutin, $C_{3.23}H_{5.31}O_{1.27}N$), is prepared by treating gelatin with sodium nitrite in acetic acid solution; it forms a light brownish-yellow resin, is readily soluble in water, less so in alcohol, gives a reddish-violet biuret reaction, and when hydrolysed by means of fuming hydrochloric acid on the water-bath, forms a fluorescent

solution. The product of hydrolysis contains oxalic acid, glycine, histidine, and arginine. Lysine, which is present as a product of the hydrolysis of gluten, is not obtained from deaminogluten; in its place there is found a *picate* which melts at 149–150° and yields a product melting at about 220°, together with a hydroxyaminovaleric acid crystallising in leaflets, and melting at 252°. The *picate* formed from this gives analytical results agreeing best with those required by the *picate* of an aminovaleric acid, $C_{11}H_{14}O_9N_4$. G. Y.

Monoamino-acids of Gluten. EMIL ABDERHALDEN and FERNAND MALENGREAU (*Zeit. physiol. Chem.*, 1906, **48**, 513–518).—The following figures are the percentages of amino-acids obtained from gliadin, the proteid of gluten of wheat which is soluble in alcohol, compared with those from gluten (or gluten-casein) which is insoluble in that reagent.

	Gluten.	Gliadin.
Glycine	0.41	0.68
Alanine	0.3	2.66
Aminovaleric acid	not found	0.33
Leucine	4.1	6.0
Proline	3.97	2.4
Glutamic acid	24.0	31.5
Aspartic acid.....	0.64	1.24
Phenylalanine	1.0	2.6
Tyrosine.....	1.9	2.37
Tryptophan	{ not	1.0 (approx.)
Serine	{ estimated.	0.12
Lysine	2.15	0.0
Histidine	1.16	1.2
Arginine	4.4	2.75

W. D. H.

Formation of Methæmoglobin. II. ALLEXIS BABEL (*Arch. Sci. phys. nat.*, 1906, [iv], **22**, 216–239).—The substances (compare this vol., i, 779) which convert oxyhæmoglobin into methæmoglobin are not acting as catalytic agents, because if care is taken to avoid secondary reactions it is not possible to recover the whole of the substance at the end of the reaction; and, further, there exists for each substance a limiting quantity below which it is incapable of effecting any change in the oxyhæmoglobin. It is probable that in the conversion of oxyhæmoglobin into methæmoglobin, hæmoglobin is formed as an intermediate product; this undergoes a molecular rearrangement owing to the toxic action of the reacting substance, and is then oxidised to methæmoglobin. M. A. W.

Oxyhæmoglobin Fluorides. ANTONY VILA and M. PIETTRE (*Bull. Soc. chim.*, 1906, [iii], **35**, 685–688. Compare Abstr., 1905, i, 847).—The first portion of the paper is polemical against Ville and Derrien (Abstr., 1905, i, 399, 500, 622), and affirms the views put forward in the authors' previous papers (Abstr., 1905, i, 399, 500,

622, 847 ; ii, 402). In the second portion it is shown that the shifting of the new absorption band of oxyhæmoglobin from $\lambda 612$ to $\lambda 634$, brought about by the addition of minute quantities of fluorides, may be used for the detection of the latter (compare Ville and Derrien, this vol., ii, 390). The optical effect is even shown when oxyhæmoglobin is added to water in which such insoluble fluorides as those of calcium, barium, or strontium have been suspended. The simultaneous presence of phosphates, however, diminishes the sensibility of this test in the case of soluble fluorides, and may completely mask it in the case of the slightly soluble fluorides. Thus fluorine cannot be detected in bone ash, teeth ash, or apatite by this method. T. A. H.

Oxidation of Nucleic Acids. I. HANS STEUDEL (*Zeit. physiol. Chem.*, 1906, 48, 425—429).—When copper nucleate is mixed with concentrated nitric acid, a vigorous action ensues ; a similar reaction, but less violent, occurs when the nitric acid is previously diluted with its own volume of water. After several days a considerable precipitate of guanine and adenine nitrates is formed. Other products of oxidation are xanthine, hypoxanthine, thymine, uracil, and oxalic acid, products which, with the exception of oxalic acid, are also formed by the hydrolytic decomposition of nucleic acid. Pure adenine gives neither Millon's reaction nor the red coloration with diazobenzene salts in alkaline solution. J. J. S.

Lecithin-sugar and Jecorin and the Physico-chemical Behaviour of Sugar in the Blood. PAUL MAYER (*Chem. Centr.*, 1906, ii, 536—537 ; from *Biochem. Zeit.*, 1906, 1, 81—107).—Lecithin-dextrose is probably a solid solution or a molecular combination of the two substances. Aqueous solutions of the substance are precipitated by sodium chloride, barium chloride, or silver nitrate. Lecithin-dextrose readily reduces an alkaline solution of copper, is fermentable, and forms an *osazone* which melts at 205° . Jecorin and lecithin-dextrose are not identical, because the sugar is firmly attached in the former compound and only loosely in the latter. The existence of a ferment in the blood which is able to split off sugar from jecorin is denied ; it is, moreover, improbable that sugar occurs in the blood combined in the form of jecorin. A physiological salt solution of jecorin activates cobra poison in just the same way as lecithin. P. H.

The Rendering Insoluble of Gelatin by Oxidation Products of Phenols. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1906, [iii], 35, 600—602).—In addition to the developers already studied (this vol., i, 614) it is found that the phenols, gallic acid, gallotannic acid, α -naphthol, β -naphthol, resorcinol, phloroglucinol and dihydroxynaphthalene possess the property of rendering gelatin insoluble in presence of air and sodium carbonate. The rapidity with which these substances render gelatin insoluble is proportional to the readiness with which they oxidise on exposure to air in alkaline solution. T. A. H.

Action of Alums and Aluminium Salts on Gelatin. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1906, [iii], 35, 676—681).—Freshly-precipitated alumina and the various salts of aluminium possess the property of raising the “setting” temperature of gelatin solutions. This effect is due to the alumina, since different quantities of the various salts produce the same rise in the “setting” temperature so long as they yield the same quantity of alumina. The “setting” temperature increases proportionately with the quantity of aluminum salt until the equivalent of 0.64 gram of alumina per 100 grams of gelatin has been added. Further additions have at first no effect on the “setting” temperature, but finally cause it to fall. Gelatin is able to fix alumina, and when the latter is applied in the form of a salt, subsequent washing with water appears to dissociate the salt and remove the acid, leaving what is apparently a compound of gelatin and alumina in which the maximum possible amount of the latter present is 3.6 per cent. by weight.

T. A. H.

Peptones from Casein. ZDENKO H. SKRAUP and R. WITT (*Monatsh.*, 1906, 27, 663—684. Compare Skraup and Zwerger, this vol., i, 123; Kossel, *Abstr.*, 1902, i, 128; Siegfried, *Abstr.*, 1903, i, 586; 1904, i, 953; 1905, i, 104).—The authors have repeated the investigation of Siegfried’s caseinokyrine, the isolation of the kyrine being carried out under the conditions described by Siegfried. The results obtained are similar to those of Skraup and Zwerger (*loc. cit.*). The phosphotungstate of the supposed kyrine, on being fractionally extracted with 80 per cent. alcohol, yields a series of salts of different solubilities, most of which are thrown down on addition of water; the alcoholic filtrates react with picric acid, forming lysine picrate. Siegfried’s caseinokyrine sulphate is free lysine.

When dissolved in dilute acetic acid and hydrolysed with 12 per cent. hydrochloric acid, casein yields a laevorotatory solution which becomes less active, but not dextrorotatory, and contains two peptones. Of these, one is precipitated by potassium mercuric iodide, contains relatively much tyrosine, histidine 0.9, arginine 1.4, and lysine 2.2 per cent. The second is precipitated by picric acid, but not by potassium mercuric iodide, contains relatively little tyrosine, histidine 2.0, and lysine 3.0 per cent., but no arginine. Both peptones give a red biuret reaction, and are precipitated from their solutions in dilute sulphuric acid on addition of a saturated solution of ammonium sulphate.

G. Y.

Decomposition of Proteid. MAX DENNSTEDT and F. HASSLER (*Zeit. physiol. Chem.*, 1906, 48, 489—504).—An unfinished piece of work on the primary hydrolytic products (proteoses and peptones) prepared from zein, the alcohol-soluble proteid of maize. The authors’ view is that the formation of such substances is not due to simple hydrolysis, but that there is also oxidation leading to the splitting off of some of the nitrogen as ammonia, and some of the sulphur as hydrogen sulphide.

W. D. H.

Influence of Light on Ferments (Invertase) in the Absence of Oxygen. A. JODLBAUER and HERMANN VON TAPPEINER (*Chem. Centr.*, 1906, ii, 693; from *Münch. med. Woch.*, 53, 653).—The influence of sunlight on the action of invertase has been examined by operating in quartz vessels which transmit ultra-violet rays. The action is measurably retarded in an atmosphere of hydrogen, nitrogen, or carbon dioxide. The retarding influence of light is not increased in an atmosphere free from oxygen when fluorescent substances are added to the solution. This result is quite different from that obtained in the presence of oxygen; in this case, fluorescent substances increase the effect of illumination many times. H. M. D.

Diastase. I. Preparation and Properties. SIGMUND FRÄNKEL and MAX HAMBURG (*Beitr. chem. Physiol. Path.*, 1906, 8, 389—398).—The diastatic power of the malt extract is determined, and then a clear solution of basic lead acetate is added so long as the diastatic power shows no appreciable diminution. After filtration, the clear liquid should not yield a precipitate with ammonium sulphide. The liquid is passed through a Pukal filter into sterilised flasks, and is inoculated with a pure culture of Froberg yeast, which has been previously grown in a medium rich in diastase and poor in sugar. After fermentation is completed, the liquid is drawn again through a Pukal filter into a sterilised vacuum apparatus, and is distilled under a pressure of 10 mm. until the volume is some 500 c.c. It is then fermented by a mixture of Froberg and Logos yeasts, again filtered, and evaporated under reduced pressure, when a syrup is obtained. When dried over sulphuric acid, this forms a powder which is free from reducing or fermentable sugars and also from albumins.

The precipitation of calcium phosphate or barium sulphate in a solution of pure diastase carries down only a minute portion of the enzyme; shaking with aluminium hydroxide has the same effect. The enzyme may be completely removed from solution by the addition of colloidal ferric hydroxide, but its activity appears to be destroyed at the same time.

During electrolysis, diastase does not collect around the anode or cathode; it is, however, a colloid, as has been proved by means of the ultra-microscope. The diastase appears to be a mixture of various enzymes, and when dialysed into spring water it is largely separated into sugar forming enzymes which pass into the water and liquefying enzymes which remain within the dialysing membrane. Many organic solvents, such as alcohol or acetone, rapidly destroy the activity of pure diastase. J. J. S.

Reversible Enzyme Action. Formation and Decomposition of Esters by Pancreatic Enzymes. HENRI POTTEVIN (*Bull. Soc. chim.*, 1906, [iii], 35, 693—696).—Most of the facts recorded have been given already in *Abstr.*, 1903, ii, 439, 494; 1904, i, 284. It is now shown that under suitable conditions of temperature and concentration oleates of propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, and *tert*-butyl are produced by the action of the pancreatic ferment on mixtures of the appropriate alcohols with oleic acid. T. A. H.

Action of Emulsin on β -Glucosides. HUGH RYAN and GEORGE EBRILL (*Proc. Roy. Irish Acad.*, 1906, **26**, B, 53—55. Compare Abstr., 1904, i, 223).—The authors have tested the action of emulsin on β -*o*-tolyl arabinoside, β -carvacryl arabinoside, $\beta\beta$ -naphthyl arabinoside, and β -phenyl glucoside. The last compound was almost completely converted into phenol and dextrose, but in the case of the arabinosides, although faint odours of carvacrol and cresol were observed, there was no indication of even a trace of arabinose.

A table is given showing those synthetical glucosides which are hydrolysed and those which are not hydrolysed by emulsin. It is seen that the activity of emulsin towards a glucoside depends not only on the configuration of the molecule, as Fischer pointed out, but also on the nature of the groups. Thus the replacement of four hydrogen atoms in $\beta\beta$ -naphthyl glucoside by four acetyl groups converts a glucoside hydrolysable by emulsin into one which cannot be so hydrolysed; the conversion of salicin into its benzoyl derivative, populin, has a similar effect. T. H. P.

Action of Lipase. ALONZO E. TAYLOR (*J. Biol. Chem.*, 1906, **2**, 87—104. Compare Kastle and Loevenhart, Abstr., 1901, i, 178; Kastle, Johnston, and Elove, *ibid.*, 1904, i, 702).—All the experiments have been made with the powder obtained by repeatedly extracting castor beans with dry ether and crushing. This powder contains lipase, amylase, invertase, maltase, and an endotrypsin, but not any peroxydase. It is possible to separate lipase from the other enzymes, but the product is then much less stable. With water it forms a cloudy emulsion, and when repeatedly filtered loses its activity. When dry it may be heated above 100° without injury. Its activity is not destroyed by free acid, but when heated with water the enzyme is hydrolysed. Its action on triacetin has been studied; it has a markedly accelerating effect on the hydrolysis. The reverse process, conversion of glycerol and acetic acid into triacetin, has a very low velocity and for all practical purposes may be neglected, although in the hydrolysis a state of equilibrium is established. This equilibrium mixture has practically the same composition as the mixture formed when acids are used in the hydrolysis.

The results obtained for the hydrolysis agree with those for a unimolecular reaction and the ratio $V_{t_n} + 10^\circ / V_{t_n} = 2.6$ between 18° and 28°.

In the case of triolein, Henri and Nieloux's results (*Compt. rend. Soc. Biol.*, 1904, **67**, 175) have been confirmed, namely, that t/x is constant. In this reaction the temperature coefficient is small, as an increase of 10° produces an increase of only some 20 per cent. in the velocity. The velocity measured in this case of a two-phase system is thought to be the diffusion velocity, and not the velocity of the chemical reaction. J. J. S.

Fission of Lipoid Substances by Lipase and the Optical Antipodes of Natural Lecithin. PAUL MAYER (*Chem. Centr.*, 1906, ii, 493—494; from *Biochem. Zeit.*, 1906, **1**, 39—52).—Lecithin, jecorin, and protagon are readily split up by lipase; the reaction takes place in

neutral solution, but less readily than in faintly acid solution. Gastric juice has no action on these substances. Ordinary dextrorotatory lecithin, when heated in a sealed tube with ten times the quantity of methyl alcohol for five or six hours at 90—100°, yields inactive lecithin in a form which is partly crystalline and partly pasty; this substance is soluble in alcohol, ether, light petroleum, or chloroform, and is only slightly soluble in acetone; when freshly prepared it is light yellow, but it soon darkens. 1-*Lecithin*, which is obtained by the action of steapsin on inactive lecithin, has $[\alpha]_D - 8.59^\circ$. d-*Glycerophosphoric acid*, which is formed at the same time by the action of the lipase on the d-lecithin in the inactive mixture, forms white flakes and has $[\alpha]_D - 1.04^\circ$.
P. H.

Nature and Effects of Rennet Coagulation. III. KARL SPIRO (*Beitr. chem. Physiol. Path.*, 1906, 8, 365—369. Compare this vol., i, 127).—In the precipitation of cheese, free hydrogen ions are produced as in the precipitation of paracasein. The formation of cheese depends on both temperature and amount of calcium ion.

Pure casein is decomposed by rennin in a very short time, yielding albumoses. This proteolysis is not due to pepsin mixed with the rennin.
J. J. S.

Specific Action of Peroxydases as Enzymes. ALEXIS BACH (*Ber.*, 1906, 39, 3329—3331. Compare this vol., i, 616).—A reply to Chodat's claim for priority (this vol., i, 779). The so-called Chodat-Bach theory was suggested simultaneously by Engler and Bach.

G. Y.

Lactic Acid Fermentation. EDUARD BUCHNER and JAKOB MEISENHEIMER (*Annalen*, 1906, 349, 125—139).—The amount of zinc lactate obtained, and not that of the carbon dioxide liberated from calcium carbonate, must be taken as the measure of the lactic acid formed by fermentation; 2.1 and 1.25 grams respectively of zinc lactate have been obtained by the action of 10 grams each of two further enzyme preparations from *Bacillus Delbrücki* (compare Abstr., 1903, ii, 318). The enzymes become ineffective if during the preparation the heating is carried out at 90—92° for one hour. In all experiments the bacteria were killed by treatment with toluene, the resulting preparations causing neither growth nor acidification in contact with sterilised tubers at 45° for eight weeks.

It may be now considered certain that the lactic acid fermentation of sugar is caused by the action of an enzyme, the lactic acid bacteriozymase, which is a product of the living lactic acid bacteria and can be separated from it; the lactic acid is decomposed in the second stage to carbon dioxide and alcohol by the lactacidase.

A series of experiments were made with the expressed juices of *Bacillus Delbrücki*; these were not capable of forming lactic acid from sugar, the fermentative agent remaining in the residue from the expression.

As the enzyme preparation from *Bacillus Delbrücki* ferments maltose as well as sucrose, the presence of a hydrolytic enzyme must be assumed. In both cases inactive lactic acid is formed.

A 10 per cent. solution of sucrose, when treated with the enzyme preparation at 35° for one hour, has a faint reducing action towards Fehling's solution.

As both *d*- and *l*-lactic acid have been obtained by treating maltose with the living bacillus, and *d*-lactic acid has been formed in the same manner from sucrose, it is evident that the nature of the product depends on some condition such as the length of time of the fermentation, the presence of calcium carbonate, or the nature of the culture medium. G. Y.

Acetic Acid Fermentation. EDUARD BUCHNER and RUFUS GAUNT (*Annalen*, 1906, **349**, 140—184. Compare preceding abstract; Buchner and Meisenheimer, *Abstr.*, 1903, ii, 318).—The paper opens with an account of the work of previous authors on the acetic acid fermentation of alcohol.

The activity of nine separate enzyme preparations from beer-vinegar bacteria prepared by Buchner and Meisenheimer's method was tested. The comparative activity depends on the uniformity of the acetone treatment, the genesis of the culture, and the temperature at which the pure culture is grown on the tubers; 100 grams of the most active preparation, obtained from about 220 grams of the living bacteria containing 55 per cent. of water, produced 4 grams of acetic acid. Finely powdering the enzyme does not alter the oxidising effect. Active preparations, obtained when the centrifuged, living bacteria were dried on a porous plate before being added to the acetone, were not sterile; sterility is produced only by adding the still moist bacteria to the acetone and treating the enzyme with toluene.

In two experiments, propyl alcohol was oxidised to propionic acid by the enzyme preparation from beer-vinegar bacteria. It may be regarded as certain that the acetic acid fermentation of alcohol is caused by an enzyme, to be called the alcohol-oxydase, which is a product of the vinegar bacillus. The ash of the bacteria contains an amount of iron equivalent to 0.08 per cent. of the enzyme preparation, which in alcoholic guaiacum resin solution gives a transient coloration with hydrogen peroxide.

The relation of the alcohol-oxydase to other known oxidising enzymes is discussed.

The expressed juice of the beer-vinegar bacteria does not oxidise alcohol in the presence of air (compare preceding abstract).

The results of the experiments described are given in a series of tables. G. Y.

Organic Chemistry.

Alkaline Aqueous Mercuri-iodide as a Reagent for Hydroxyl Groups. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1906, **244**, 373—375).—When boiled for one minute with Nessler's solution, substances which contain a primary or a secondary alcohol group bring about a reduction of the solution (to metallic mercury). Substances containing a tertiary alcoholic group do not effect this reduction. The action of substances containing phenolic groups is varied.

Sachsse's (alkaline mercuri-iodide) solution reacts in the same way, but not Knapp's (alkaline mercuricyanide) solution. C. F. B.

Preparation of Chemically Pure Methyl and Ethyl Alcohols; their Specific Gravities. PETER KLASON and EVERT NORLIN (*Arkiv Kem. Min. Geol.*, 1906, **2**, No. 24, 1—7).—Chemically pure methyl or ethyl alcohol may be prepared as follows: 500 grams of pure potassium methyl (or ethyl) sulphate are dissolved in water, and to the solution rather more than the calculated quantity of pure sulphuric acid is added, the whole liquid measuring about 2 litres. The methyl (or ethyl) alcohol is distilled in a current of steam and concentrated by fractionation, finally, from ignited potassium hydroxide. To remove the last traces of moisture, freshly ignited lime (from marble) and, finally, calcium are used. Distillation from calcium is continued until the specific gravity of the alcohol undergoes no further change.

Pure methyl alcohol has the sp. gr. 0.796472 at 15°/15°, and, between 0° and 30°, the sp. gr. at $t^{\circ}/4^{\circ}$ is expressed by $0.80999 - 0.00093 t - 0.00000025 t^2$.

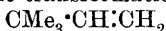
Pure ethyl alcohol has the sp. gr. 0.794130 at 15°/15°; the value 0.79429, on which Windisch's tables are calculated, indicates that the alcohol used by this author contained 0.05 per cent. of water. Its sp. gr. at 0°/4° is 0.80628; at 10°/4°, 0.79792; at 20°/4°, 0.78938; at 30°/4°, 0.78080. These values agree well with those obtained by Winkler.

T. H. P.

sec.- and *tert.*-Pinacolyl Alcohols and their Separation. MAURICE DELACRE (*Bull. Soc. chim.*, 1906, [iii], **35**, 811—816. Compare this vol., i, 476, 518, 551, 784).—*tert.*-Pinacolyl alcohol was obtained by the application of the Grignard reaction to isopropyl bromide. Its odour is similar to that of the alcohol prepared from pinacolin, and after the removal of traces of impurity by shaking it with solid potassium hydroxide, it boils at 118.4—119.2° under 748 mm. pressure and freezes about 10.5°. The chloride boils from 112—113.4° and solidifies at 7°; the acetate, obtained by warming the alcohol with acetic anhydride for several hours, boils from 125—140°. When the alcohol is heated with the anhydride in a closed tube for three days at 200°, the principal product is tetramethylethylene

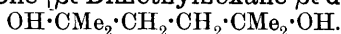
($\beta\gamma$ -dimethyl- Δ^2 -butylene). The *tert.*-pinacolyl alcohol (and also the alcohol regenerated from the acetate described above) is dehydrated by dilute sulphuric acid much more rapidly than the alcohol obtained from pinacolin, and this method may be used for their separation.

The synthetic *tert.*-pinacolyl alcohol and the alcohol obtained from pinacolin appear therefore to be distinct substances possessing different physical properties, but yielding the same derivatives (chloride, bromide, acetate). The formation of the same derivatives from the two alcohols is similar to the transformation of the group

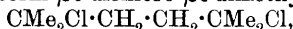


into $\text{CMe}_3\cdot\text{CMe}_2$ by the action of hydrogen bromide on $\gamma\gamma$ -dimethyl- Δ^2 -butylene (this vol., i, 477).
T. A. H.

Succinic Pinacone [$\beta\epsilon$ -Dimethylhexane- $\beta\epsilon$ -diol],

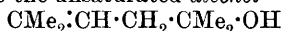


LOUIS HENRY (*Compt. rend.*, 1906, 143, 496—500).— $\beta\epsilon$ -Dimethylhexane- $\beta\epsilon$ -diol (compare Zelinsky, *Abstr.*, 1902, i, 593; and Valeur, *Bull. Soc. chim.*, 1902, 27, 1139), readily obtained by the action of magnesium methyl bromide on ethyl lævulate, behaves like a tertiary alcohol (this vol., i, 133, 329), and reacts with fuming hydrochloric acid or acetyl chloride to form $\beta\epsilon$ -dichloro- $\beta\epsilon$ -dimethylhexane,



which crystallises in plates or needles melting at 66 — 67° , boils and decomposes at 180° , and is identical with the compound obtained by the action of hydrochloric acid on diisocrotonyl or diisobutenyl (Pogorzelsky, *Abstr.*, 1899, i, 785). $\beta\epsilon$ -Dimethylhexane- $\beta\epsilon$ -diol is readily dehydrated by the action of dilute sulphuric acid even in the

cold to form *s*-tetramethyltetramethylene oxide, $\begin{matrix} \text{CH}_2\cdot\text{CMe}_2 \\ | \\ \text{CH}_2\cdot\text{CMe}_2 \end{matrix} > \text{O}$ (compare Pogorzelsky, *Abstr.*, 1899, i, 785), which is a colourless, mobile liquid with an agreeable odour, boils at 116 — 117° , and reacts even in the cold with fuming hydrochloric acid to form $\beta\epsilon$ -dichloro- $\beta\epsilon$ -dimethylhexane. When $\beta\epsilon$ -dimethylhexane- $\beta\epsilon$ -diol is distilled, it suffers partial dehydration and forms the unsaturated alcohol



[$\beta\epsilon$ -dimethyl- Δ^2 -hexylene- β -ol], which is a colourless, mobile liquid with an agreeable penetrating odour, boils at 165° , combines readily with bromine, and is converted into its chloride by the action of acetyl chloride.
M. A. W.

Distillation of Ether. E. J. SWAAB (*Chem. Centr.*, 1906, ii, 841; from *Pharm. Weekblad*, 1906, 43, 817—818).—A glass attachment is described, enabling a reflux condenser to be used, the condensed ether passing down a vertical tube into the receiver, the vapour entering by means of a side branch.
P. H.

Freezing and Melting Points of Glyceryl Nitrate. HERMANN KAST (*Chem. Centr.*, 1906, ii, 948; from *Zeit. ges. Schiess. Sprengstoffwesen*, 1, 225—228).—Glyceryl nitrate exists in two modifications. The labile form melts at 2.8 — 2.9° and solidifies at 2.0 — 2.2° , whilst the stable form melts at 13.1 — 13.2° and solidifies at 12.5° . The labile

form has a more glassy appearance than the other. It is very difficult to freeze small quantities, but less so to freeze large quantities, of glyceryl nitrate; in a mixture of ether and carbon dioxide it solidifies to an amorphous mass which, however, becomes liquid on warming to temperatures below the true freezing point; when once it has been frozen it is less difficult to freeze it a second time. The depression of the freezing point of glyceryl nitrate by dinitrochlorohydrin agrees fairly closely with Raoult's law.

P. H.

Origin of Optically Active Fatty Acids in Nature. CARL NEUBERG (*Chem. Centr.*, 1906, ii, 1132—1133; from *Biochem. Zeit.*, 1906, 1, 368—379).—The author has obtained experimental evidence in support of his theory that mineral oil originates from the optically active decomposition products of proteids. The fatty acids isolated from a sample of putrid cheese yielded a fraction comprising from acetic to hexoic acid which had $\alpha_D + 1.2^\circ$. The volatile acids obtained from putrid gelatin were similarly active, but to a less degree. Further, by the action of lipase from vegetable sources on the triglyceride of dibromostearic acid, free dextrorotatory dibromostearic acid and a dextrorotatory glyceride were obtained, showing that as a result of slow oxidation and asymmetric fission by living or unorganised ferments, inactive fats may give rise to optically active substances.

P. H.

Active Components of α -Bromopropionic Acid. LUDWIG RAMBERG (*Annalen*, 1906, 349, 324—332. Compare Abstr., 1901, i, 63; Warburg and Fischer, Abstr., 1905, i, 692).—The resolution of the inactive acid can be effected without great loss of material by a method involving fractional crystallisation of the cinchonine salt and "freezing" out the inactive acid from the active acids so obtained. A supersaturated solution of the salt, $C_{19}H_{22}ON_2 \cdot 2C_3H_5O_2Br$, is made by dissolving 153 grams of the acid and 148 grams of cinchonine in 3 litres of water at $30-35^\circ$, the last 25 per cent. of the acid being added slowly after the base has dissolved. After evaporating the solution at $27-30^\circ$ in a vacuum to 2,300 c.c., the crystals (fraction I.) are removed and the mother liquor evaporated to about 1,400 c.c. and the second crop of crystals (fraction II.) filtered off. The solution of these crystals is employed in dissolving a fresh quantity of cinchonine and of the racemic acid. The acid from fraction I. ($\alpha_D - 11^\circ$) and that from the mother liquor from fraction II. ($\alpha_D + 19^\circ$) are treated separately as follows. The temperature is raised to the highest at which crystallisation will begin, the acid is nucleated with a crystal of the racemic form, and the temperature allowed to fall very slowly for several days. When half the acid has solidified, the crystals are separated centrifugally, and consist of the pure racemic form. The liquid is again nucleated and cooled slowly to 0° , whereby a further quantity of the racemic form is obtained. The acid which still remains liquid has $\alpha_D \pm 33^\circ$, and after a third nucleation at -5° , cooling to -15° , and removal of the crystals, has $\alpha_D \pm 38^\circ$. The cinchonine salt of this acid is recrystallised six or eight times from water or acetone. The recovered *l*- α -bromopropionic acid solidifies completely at -40° ;

when the temperature is raised slowly to -7° and then lowered to -12° , the crystals obtained, after removal of the liquid portion, consist of the pure *lævo*-acid. It melts at -6° to -7° , has a sp. gr. 1.708 at $20^{\circ}/20^{\circ}$, and $[\alpha]_D -27^{\circ}$ at 20° (compare Warburg, *loc. cit.*). The pure *d*-acid has not been obtained; the *ethyl* ester of an acid having $\alpha_D +36.33^{\circ}$ boils at $62-63^{\circ}$ under 15 mm. pressure, has a sp. gr. 1.388 at $20^{\circ}/4^{\circ}$, and $\alpha_D +36.35^{\circ}$ at 20° . The pure ester should have $\alpha_D +46^{\circ}$ and $[\alpha]_D +33^{\circ}$ at 20° (compare Walker, *Trans.*, 1895, **67**, 921). C. S.

Theory of Saponification. JULIUS MARCUSSON (*Ber.*, 1906, **39**, 3466—3474).—According to Lewkowitsch (*Proc.*, 1899, **15**, 190) incompletely hydrolysed fats should contain mono- and di-glycerides, and the presence of these substances should be indicated by a high acetyl value; but as other compounds, such as hydroxy-acids, lactones, &c., are also indicated by the acetyl value, the author has endeavoured to isolate the lower glycerides and thus obtain further support for the theory of successive hydrolysis.

A quantity of incompletely saponified fat was divided into two equal parts. One was acidified, and the precipitated neutral fat and free fatty acid acetylated directly; from the other portion, after removing excess of alkali with acid, the soaps were extracted and the residual neutral fat acetylated. Finally, the fatty acids from the soaps of the second portion were acetylated. The anticipated increase in the acetyl value was never observed. The portion containing both neutral fat and free fatty acid usually gave a slightly higher acetyl value than that of the neutral fat, and the acetyl value of the separated acids were sometimes as high as, and sometimes higher than, that of the neutral fat. These results do not point to the existence of the lower glycerides, but seem to depend on certain changes which have occurred in the fatty acids.

The saponification of olive oil by shaking with concentrated aqueous sodium hydroxide in stoppered vessels excludes the interference of atmospheric oxygen and affords scope for the hydrolysis to occur in successive stages, but no indication of the formation of the lower glycerides was obtained. Saponification of this oil in the cold with the enzyme of castor oil seeds gave no indication of successive hydrolysis. The hydrolytic changes which occur in rancid fats do not give rise to the lower glycerides, for although di-rucenin is found in old rape-seed oil, yet it only occurs in the oil which has been refined with sulphuric acid, and in all probability arises as a fission product of tri-rucenin, formed, not by alkaline hydrolysis, but by the action of the acid. The examination of rancid sheep's tallow and olive oil gave no indubitable evidence of the presence of mono- and di-glycerides.

G. T. M.

Beeswax from Annam. J. BELLIER (*Ann. Chim. anal.*, 1906, **11**, 366—368).—A sample of yellow beeswax received from Annam gave results, on analysis, which differed considerably from those yielded by ordinary European beeswax. The figures obtained were: sp. gr. 0.964; m. p. 61° ; acid number, 7.8; ester number, 86.6; iodine number, 6; unsaponifiable matter, 10.5 per cent. W. P. S.

Historical Note on the Fixation of Ozone by Oleic Acid. THEODOR WEYL (*Ber.*, 1906, 39, 3347—3348).—The author claims to have been the first to observe the fixation of ozone by acids of the oleic series (compare Molinari, this vol., i, 792; Harries, *ibid.*, i, 793).
E. F. A.

Separation of the Fatty Acids of Cod-liver Oil. HENDRIK BULL (*Ber.*, 1906, 39, 3570—3576. Compare Abstr., 1900, ii, 250, 325; 1901, ii, 137; Ljubarsky, Abstr., 1898, ii, 299).—The fatty acids of cod-liver oil are separated by conversion into the methyl esters, fractional distillation of these under 10 mm. pressure, when 80 per cent. of the esters distil below 240°, and hydrolysis of the fractions so obtained. In this manner have been isolated myristic, palmitic, stearic, oleic, and erucic acids, as also two new acids, $C_{16}H_{30}O_2$, and $C_{20}H_{38}O_2$.

The unsaturated acid $C_{16}H_{30}O_2$, which is present to the extent of 6 per cent. of the cod-liver oil, and is obtained also from herring and whale oils, melts at -1° , has an acid number 219, and an iodine number 91.5, forms a *methyl* ester boiling at 185—186° under 10 mm. pressure, and on oxidation with potassium permanganate in alkaline solution cooled with ice, yields a *dihydroxypalmitic acid* crystallising in white leaflets and melting at 125°. The *acetyl* derivative of this acid has an acetyl number 355.7.

Gadoleic acid, $C_{20}H_{38}O_2$, obtained together with stearic and oleic acids on hydrolysis of the fraction boiling at 205—206° under 10 mm. pressure, occurs also in herring and whale oils; it melts at 24.5° , and has an acid number 180.5, and an iodine number 80.3. On oxidation with potassium permanganate in alkaline solution cooled with ice, it yields *dihydroxygadoleic acid*, $C_{20}H_{38}O_2(OH)_2$, which separates from alcohol in white crystals, melts at 127.5—128°, and has an acid number 161.7.

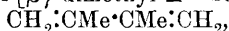
Heyerdahl's jecoleic acid (*Cod-liver Oil and its Chemistry*), if present, can be so only in very small amount, whilst this author's dihydroxy-acid is probably a eutectic compound of oleic and gadoleic acids.

G. Y.

Action of Alkali Carbonates on $\beta\gamma$ -Dibromo- $\alpha\alpha$ -dimethyl Acids. Part II. ALFRED COURTOT (*Bull. Soc. chim.*, 1906, [iii], 35, 969—988. Compare this vol., i, 788).— $\beta\gamma$ -Dibromo- $\alpha\alpha\beta$ -trimethylbutyric acid, on treatment with zinc dust, furnishes dimethylisopropenylacetic [$\alpha\alpha$ -dimethyl- β -methylenebutyric] acid, and reacts with a dilute solution of potassium hydrogen carbonate, forming dimethylisopropenylcarbinol. With potassium carbonate the action proceeds further, and in addition to the alcohol some pinacolin and diisopropenyl are formed. The latter is the principal product obtained when $\beta\gamma$ -dibromo- $\alpha\alpha\beta$ -trimethylbutyric acid is treated with pyridine in presence of ether.

Dimethylisopropenylcarbinol, $CH_2:CM_e \cdot CM_e \cdot OH$, is a mobile liquid of pleasant odour, melts at -17° (compare Choupotsky and Mariutza, Abstr., 1890, 727). The *phenylcarbamate* separates from boiling light petroleum in long needles and melts at 103—104°. On dehydration

with sulphuric acid, the alcohol yields a mixture of diisopropenyl and pinacolin. Diisopropenyl [$\beta\gamma$ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene],



has a sp. gr. 0.73074 at 15° , n_D^{20} 1.4379, n_D^{25} 1.4527, n_D^{30} 1.4622, and n_D^{40} 1.4421, and on oxidation with permanganate yields acetic and formic acids and a small quantity of pinacolin. The dibromide, $\text{CH}_2\text{Br:CMeBr:CMe:CH}_2$, melts at 49° , boils at 105° under 14 mm. pressure, and regenerates the hydrocarbon on treatment with magnesium in presence of ether (compare Kondakoff, Abstr., 1901, i, 62). The tetrabromide melts at 140° [compare (1) Mariutza and (2) Kondakoff (*loc. cit.*)]. The oily bromide referred to by Kondakoff (*loc. cit.*) boils at 115° under 14 mm. pressure, and is probably a mixture of the dibromide with other more highly brominated derivatives.

Dimethylallylcarbinol, $\text{CH}_3\text{:CH:CH}_2\text{:CMe}_2\text{:OH}$, obtained by condensing acetone with allyl iodide in presence of zinc, is a mobile liquid and boils at 120° under atmospheric pressure (compare Saytzeff, Abstr., 1877, ii, 298). The *phenylcarbamate* crystallises from boiling light petroleum in slender needles and melts at $49\text{--}50^\circ$.

When ethyl methylacrylate reacts with magnesium methyl iodide, dimethylisopropenylcarbinol, diisopropenyl, and *aa*-methylethylacetone [*methyl α -methylpropyl ketone*] are produced (compare Kohler, Abstr., 1904, i, 595). *aa*-Methylethylacetone may also be prepared by treating ethyl acetoacetate with ethyl and methyl iodides successively in presence of sodium and alcohol and hydrolysing the complex ester so formed. The ketone is liquid, has a penetrating camphoraceous odour, and boils at 116° under atmospheric pressure; the *semicarbazone* crystallises from ether and melts at $95\text{--}96^\circ$; the *oxime* is a pungent smelling liquid and boils at 89° under 20 mm. pressure; the *phenylhydrazone* is viscid and boils at 152° under 10 mm. pressure.

Diethylisopropenylcarbinol, $\text{CH}_3\text{:CMe:CMe}_2\text{:OH}$, the sole product of the action of magnesium ethyl iodide on ethyl methylacrylate, is a mobile liquid with a camphoraceous odour and boils at 152° .

Methylpropenylcarbinol, CHMe:CHMe:CH:OH , the sole product of the action of magnesium methyl iodide on crotonaldehyde, boils at 122° under atmospheric pressure (compare Grignard, Abstr., 1901, i, 679); the *acetate* boils at 138° , and the *phenylcarbamate* crystallises from light petroleum and melts at 43° .

By the action of magnesium methyl iodide on ethyl $\beta\beta$ -dimethylacrylate, dimethylpentadiene, dimethylisobutenylcarbinol, and a *ketone* yielding a *semicarbazone* crystallising in long needles and melting at $123\text{--}124^\circ$ are obtained. This ketone may be ψ -butylacetone, $\text{CMe}_3\text{:CH}_2\text{:CMe}$. Attempts to synthesise ψ -butylacetone by condensing *tert.*-butyl chloride with trioxymethylene in presence of magnesium yielded only Tissier's alcohol, $\text{CMe}_3\text{:CH}_2\text{:OH}$. The *iodide* prepared from the latter, by condensation with acetyl chloride in presence of zinc, yielded only traces of the ketone sought, and similarly attempts to prepare the ketone from ethylacetoacetate were unsuccessful.

Dimethylisobutenylcarbinol, $\text{CMe}_2\text{:CH:CMe}_2\text{:OH}$, is the principal product of the interaction of magnesium methyl iodide and ethyl methylacrylate. It has a camphoraceous odour and boils at 138° under atmospheric pressure (compare von Fellenberg, Abstr., 1904,

i, 961). The *phenylcarbamate* crystallises in silky needles and melts at 111° . $\beta\delta$ -Dimethyl- $\Delta^{\alpha\gamma}$ -pentadiene, $\text{CMe}_2\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}_2$, also produced in the above reaction (compare Grignard, Abstr., 1900, i, 382), boils at 90° under atmospheric pressure; the *dibromide* has an irritating odour and boils at 65° under 10 mm. pressure.

The foregoing results show that the fixation of magnesium alkyl haloids by the $\alpha\beta$ -unsaturated esters of the aliphatic series is confined to magnesium methyl iodide, and in this respect differ from those obtained by Kohler (Abstr., 1904, i, 595) and by Kohler and Heritage (Abstr., 1905, i, 207) with unsaturated compounds of the cyclic series.

When $\beta\gamma$ -dibromo- β -phenyl- $\alpha\alpha$ -dimethylbutyric acid is treated with an aqueous solution of potassium carbonate, β -hydroxy- β -phenyl- $\alpha\alpha$ -dimethylbutyrolactone, $\text{CPh}(\text{OH})\cdot\text{CMe}_2\text{---}\text{CH}_2\text{---}\text{O}>\text{CO}$, and *phenylisoprene* are produced. The former crystallises from a mixture of ether and light petroleum and melts at 115° . Phenylisoprene is a mobile odorous liquid, boils at 95° under 24 mm. pressure and yields a liquid dibromide. When dissolved in carbon disulphide and treated with bromine, it furnishes a crystalline *product* which may be a monobromo-derivative of the dibromide; it melts at 76° . T. A. H.

γ -Aldehydo-acids. EDMOND E. BLAISE and ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, [iii], 35, 989—1004. Compare Abstr., 1905, i, 562).—When $\beta\gamma$ -dibromo- $\alpha\alpha$ -dimethylbutyric acid is distilled, it decomposes, yielding γ -bromo- $\alpha\alpha$ -dimethylbutyrolactone (this vol., i, 788), and this, when boiled with quinoline, furnishes isoprene. Ethyl $\beta\gamma$ -dibromo- $\alpha\alpha$ -dimethylbutyrate, obtained by the action of bromine on ethyl dimethylvinylacetate, is readily hydrolysed either by potassium hydroxide or acetate dissolved in water, and therefore yields the same products as the free acid when treated with these reagents.

β -Bromo- $\alpha\alpha$ -dimethylvalerolactone, when heated in presence of quinoline, yields the corresponding unsaturated lactone, $\text{CH}\cdot\text{CMe}_2\text{---}\text{CH}(\text{Me})\text{---}\text{O}>\text{CO}$, and this, when dissolved in an aqueous solution of potassium hydroxide, yields mesitonic acid, $\text{CH}_2\text{Ac}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$.

$\beta\gamma$ -Dibromo- $\alpha\alpha\beta$ -trimethylbutyric acid (Abstr., 1905, i, 562) crystallises from light petroleum and melts at 107 — 108° . When heated, it furnishes first the corresponding bromolactone, $\text{CMeBr}\cdot\text{CMe}_2\text{---}\text{CH}_2\text{---}\text{O}>\text{CO}$, which crystallises in parallelopipeds and melts at 194° , and finally the unsaturated lactone, $\text{CMe}\cdot\text{CMe}_2\text{---}\text{CH}\text{---}\text{O}>\text{CO}$, which is crystalline at low temperatures, melts at -25° , boils at 65° under 12 mm. or at 174° under atmospheric pressure, and on hydrolysis (*loc. cit.*) furnishes γ -hydroxy- $\alpha\alpha\beta$ -trimethylbutyrolactone, $\text{OH}\cdot\text{CH}\cdot\text{CH}(\text{Me})\text{---}\text{CMe}_2\text{---}\text{CO}>\text{O}$. The *ethyl ether* of this is a mobile liquid and boils at 107° under 11 mm. pressure; the acetate (*loc. cit.*) boils at 135° under 11 mm. pressure. On treatment with semicarbazide hydrochloride in presence of sodium

acetate, the hydroxylactone yields *trimethylsuccinic hemialdehyde semicarbazone*, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N} : \text{CH} \cdot \text{CHMe} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$, which forms small crystals and melts and decomposes at 240° . The corresponding *oxime*, obtained in an analogous manner, melts and decomposes at 153° , and the *phenylhydrazone* melts at 110° .

On oxidation with chromic acid, γ -hydroxy- $\alpha\alpha\beta$ -trimethylbutyrolactone yields trimethylsuccinic acid.

$\beta\gamma$ -Dibromo- $\alpha\alpha\beta$ -trimethylbutyrolactone, obtained by the action of bromine on the unsaturated bromolactone mentioned previously, melts at 107 — 108° .

γ -Bromo- $\alpha\alpha$ -dimethylisopropenylacetic acid, $\text{CHBr} \cdot \text{CMe} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$, obtained by heating methyl $\beta\gamma$ -dibromo- $\alpha\alpha\beta$ -trimethylbutyrate with potassium hydroxide dissolved in water, crystallises from light petroleum and melts at 59° . Its *methyl ester*, prepared from $\beta\gamma$ -dibromo- $\alpha\alpha\beta$ -trimethylbutyrate, is a mobile liquid and boils at 104° under 19 mm. pressure.

β -Bromo- β -phenyl- $\alpha\alpha$ -dimethylbutyrolactone, obtained by heating $\beta\gamma$ -dibromo- β -phenyl- $\alpha\alpha$ -dimethylbutyric acid at 220° under 30 mm. pressure, crystallises from a mixture of ether and light petroleum in brilliant lamellæ, melts at 131° , and, when boiled with quinoline, yields *phenyldimethylbutenolide*, $\begin{array}{c} \text{CPh} \cdot \text{CMe}_2 \\ | \\ \text{CH} \end{array} \longrightarrow \text{O} > \text{CO}$, which crystallises

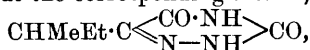
from ether, melts at 70 — 71° , boils at 145° under 10 mm. pressure, and on hydrolysis yields γ -hydroxy- β -phenyl- $\alpha\alpha$ -dimethylbutyrolactone. This forms brilliant spangles from benzene, begins to decompose at 120° , melts at 131° , and, with semicarbazide hydrochloride in presence of sodium acetate, yields *phenyldimethylsuccinic hemialdehyde semicarbazone*, which crystallises from alcohol and melts and decomposes at 220° . The corresponding *oxime* is crystalline, begins to decompose at 140° , and melts at 155° . The *hydroxylamine salt* of the oxime melts and decomposes at 130° . By the action of hydrazine hydrate on the γ -hydroxy-lactone (2 mols.), *phenyldimethylsuccinic hemialdehydeazine*, $\text{N}_2(\text{:CH} \cdot \text{CHPh} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H})_2$, is produced; it crystallises from alcohol and melts at 210° .

β -Phenyl- $\alpha\alpha$ -dimethylsuccinic acid, obtained by oxidising the hydroxylactone with chromic acid, separates from ether in small crystals and melts and decomposes at 180° .

T. A. H.

Preparation of Methyl ethylpyruvic Acid and its Derivatives. RENÉ LOCQUIN (*Bull. Soc. chim.*, 1906, [iii], 35, 962—965).—Most of the facts recorded in this paper are already given in Abstr., 1905, i, 636. Ethyl *sec.*-butylacetoacetate, prepared by the general method (Abstr., 1904, i, 646), yields with hydrazine hydrate, 3-methyl-4-*sec.*-butyl-5-pyrazolone, which crystallises from boiling benzene and melts at 158 — 159° . When ethyl *sec.*-butylacetoacetate is treated with nitrosylsulphuric acid (Bouveault and Locquin, Abstr., 1904, i, 847), it furnishes ethyl α -oximino- β -methylvalerate (Abstr., 1905, i, 636), a thick liquid which has a sp. gr. 1.042 at $0^\circ/4^\circ$. This is hydrolysed by potassium hydroxide in water and furnishes the corresponding acid (*loc. cit.*), which separates from ether in brilliant spangles and melts, sublimes, and decomposes at 160 — 161° . Further, the ethyl methyl-

ethylpyruvate, formed by treating the oximino-ester with freshly-formed nitrous acid (Bouveault and Locquin, *Abstr.*, 1905, i, 10), is a colourless liquid which has a sp. gr. 0.988, boils at 78—79° under 15 mm. pressure, and is hydrolysed less easily than its analogues. The semicarbazone separates, on cooling its solution in light petroleum, in slender needles, melts at 82—83°, and, on treatment with potassium hydroxide solution at 100°, furnishes, not the semicarbazone of methyl-ethylpyruvic acid, but the corresponding *lactam*,



which crystallises from benzene on addition of alcohol in spangles and melts at 206—207°.

Ethyl methylethylpyruvate, when heated with water in a closed tube for several hours, furnishes the acid which boils at 84° under 15 mm. pressure (?), melts at 35°, furnishes a phenylhydrazone melting at 130° and a semicarbazone which crystallises from dilute alcohol and melts at 165°.

T. A. H.

[**β-Ethoxymethylacrylic Acid**]. OSKAR EMMERLING and L. KRISTELLER (*Ber.*, 1906, **39**, 3549—3550).—β-Ethoxymethylacrylic acid, recently described by the authors (this vol., i, 623), is the same substance as that prepared lately by Tschitschibabin (this vol., i, 398).

G. T. M.

Isomorphism. JEAN HERBETTE (*Chem. Centr.*, 1906, ii, 970; from *Bull. Soc. franç. Min.*, **29**, 97—190).—By special methods of crystallisation the following new crystalline forms of previously known compounds have been obtained. (1) A rhombohedral form of thallium tartrate, $\text{C}_4\text{H}_4\text{O}_6\text{Ti}_2$ [$\alpha:c = 1:1.08534$], sp. gr. 4.8; (2) a rhombic hydrated thallium tartrate, $2\text{C}_4\text{H}_4\text{O}_6\text{Ti}_2\cdot\text{H}_2\text{O}$; these salts are completely isomorphous with the rubidium and potassium salts respectively; (3) a substance obtained by crystallising a mixture of barium chloride and bromide. For details of these compounds the original paper should be consulted.

P. H.

Action of Formaldehyde Solution on Potassium Permanganate. GEORGE B. FRANKFORTER and RODNEY M. WEST (*J. Amer. Chem. Soc.*, 1906, **28**, 1234—1238).—A study on the action of formalin on solid potassium permanganate. In order to avoid a too violent action, the powdered permanganate should be diluted with an equal bulk of sand. In order to obtain the largest possible amount of gaseous formaldehyde (which may then be absorbed in water and titrated), 50 c.c. of strong formalin should be dropped slowly (so as to take about thirty minutes) on to 200 grams of the permanganate-sand mixture. A special apparatus is described and illustrated, and two tables are given.

L. DE K.

Action of Bases on Chloral Hydrate. JOHANNES E. ENKLAAR (*Rec. trav. chim.*, 1906, **25**, 297—310).—The author has extended his investigation on the rate of decomposition of chloral hydrate by the action of bases (*Abstr.*, 1905, i, 171, 741), and in the present paper the values of the velocity coefficient are tabulated for mixtures of chloral hydrate and barium hydroxide, with and without the addition of neutral barium nitrate, chloride, acetate, propionate, or valerate. The

results show that, as in the case of the other alkali or alkali-earth hydroxides, the velocity of the reaction increases with the excess of the free base above the equivalent of the chloral hydrate employed, and is accelerated by the addition of neutral salts, equivalent quantities of different salts producing the same effect. M. A. W.

Succinaldehyde Derivatives. CARL D. HARRIES and HERMANN KRÜTZFELD (*Ber.*, 1906, 39, 3670—3677. Compare Abstr., 1901, i, 451; 1902, i, 345; this vol., i, 227; Wohl and Schweitzer, *ibid.*, i, 232).—In the preparation of succindialdehyde from its dioxime by means of nitrous gases, it is advisable to pass the gases for some time after all the oxime has dissolved, as otherwise, after neutralising with calcium carbonate and evaporating, an explosive syrup is obtained. If the gas is passed for too long a time a precipitate of succinic acid appears.

Succinaldehydedisemicarbazone, $C_6H_{12}O_2N_6 \cdot H_2O$, crystallises from water, in which it is readily soluble, in the form of six-sided prisms, melting at 188°. It dissolves readily in methyl, less readily in ethyl alcohol. The diphenylmethylhydrazone melts at 96°, and not at 86° (Henle, Abstr., 1905, i, 413).

The *di-nitrophenylhydrazone* $C_{16}H_{16}O_4N_6 \cdot H_2O$, crystallises in golden yellow needles melting at 185° and is insoluble in water.

The product $C_{10}H_{10}N_2 \cdot H_2O$, obtained by the condensation of succinaldehyde with *o*-phenylenediamine, is a yellow, amorphous powder with feebly basic properties. It melts at about 150°, but after heating at 100° is anhydrous and then melts at about 177°. It dissolves in benzene or chloroform, but is insoluble in water, alcohol or light petroleum.

Succintetramethylacetal is readily converted into its *dibromo*-derivative, $CH(OMe)_2 \cdot CHBr \cdot CHBr \cdot CH(OMe)_2$, when treated with an excess of bromine in the presence of calcium carbonate in sunlight. It is a colourless oil readily soluble in organic solvents, and when heated evolves hydrogen bromide.

Dibromosuccinaldehyde, obtained by brominating the aldehyde in chloroform solution in the presence of calcium carbonate, is a yellow oil with a strong odour. It readily reduces Fehling's solution, but does not give the pyrrole reaction. When dissolved in warm acetic acid and precipitated with water, it is converted into a solid modification melting at 75° after sintering at about 50°.

When distilled under reduced pressure, the dibromo-derivative is converted into *bromofumaraldehyde*, which distils at 130° under 15 mm. pressure. The *tetra-acetal* distils at 110—120° under 15 mm. pressure.

J. J. S.

Thio-derivatives of Ketones. III. EMIL FROMM and PAUL ZIERSCH (*Ber.*, 1906, 39, 3599—3609. Compare Baumann and Fromm, Abstr., 1890, 26; 1895, i, 362; Fromm and Mangler, Abstr., 1901, i, 184).—1:3-Diketones react with hydrogen sulphide in presence of hydrogen chloride, forming thio-derivatives of the bisdiketones.

Tetrathiobisacetylacetone, $S \begin{array}{c} \diagup CMe \cdot CH_2 \cdot CMe \\ > S < \\ \diagdown CMe \cdot CH_2 \cdot CMe \end{array} S$, separates from

boiling alcohol in white crystals, melts at 161° , remains unchanged when boiled with alcoholic potassium hydroxide, or when distilled alone or with zinc dust or copper powder, dissolves in concentrated sulphuric acid and is reprecipitated on dilution, and reacts with bromine in chloroform solution, evolving hydrogen bromide and forming an unstable crystalline substance. When heated with methyl iodide at 100° , it yields trimethylsulphine iodide.

With hydrogen sulphide methylacetylacetone yields two products:

trithio-oxybismethylacetylacetone, $\text{S} \begin{array}{c} \text{CMe} \cdot \text{CHMe} \cdot \text{CMe} \\ > \text{S} \\ \text{CMe} \cdot \text{CHMe} \cdot \text{CMe} \end{array} \text{S} \begin{array}{c} \text{CMe} \cdot \text{CHMe} \cdot \text{CMe} \\ > \text{S} \\ \text{CMe} \cdot \text{CHMe} \cdot \text{CMe} \end{array} \text{O}$, which melts at 100° , is readily soluble in chloroform or alcohol, and is obtained only in a slightly impure condition, and *trithiobismethylacetylacetone*, $\text{S} \begin{array}{c} \text{CMe} \cdot \text{CHMe} \cdot \text{C}(\text{CH}_3)_2 \\ > \text{S} \\ \text{CMe} \cdot \text{CHMe} \cdot \text{C}(\text{CH}_3)_2 \end{array} \text{S}$, or $\text{S} \begin{array}{c} \text{CMe} \cdot \text{CMe} \cdot \text{CMe} \\ > \text{S} \\ \text{CMe} \cdot \text{CMe} \cdot \text{CMe} \end{array} \text{S}$, which is precipitated on addition of alcohol to its solution in chloroform and melts at 193° .

Tetrathiobisdimethylacetylacetone, $\text{S} \begin{array}{c} \text{CMe} \cdot \text{CMe}_2 \cdot \text{CMe} \\ > \text{S} \\ \text{CMe} \cdot \text{CMe}_2 \cdot \text{CMe} \end{array} \text{S} \begin{array}{c} \text{CMe} \cdot \text{CMe}_2 \cdot \text{CMe} \\ > \text{S} \\ \text{CMe} \cdot \text{CMe}_2 \cdot \text{CMe} \end{array} \text{S}$, melts at

227° , and is soluble in chloroform, but insoluble in alcohol.

These thio-derivatives of the 1:3-diketones are oxidised by shaking the benzene solution with concentrated aqueous potassium permanganate and dilute sulphuric acid.

Tetrathiobisacetylacetone yields two oxidation products: *trithio-tetraoxybisacetylacetone*, $\text{C}_8\text{H}_{14}\text{O}_4\text{S}_3$, melts at 275° , is soluble in hot water, but is almost insoluble in cold water or alcohol, and is decomposed by aqueous alkali hydroxides. *Trithiotrioxabisacetylacetone*, $\text{C}_8\text{H}_{14}\text{O}_3\text{S}_3$, crystallises from water in which it is more soluble than the tetrathiotetraoxy-compound, and melts at 225° . On further oxidation, the two preceding substances yield *trithiopentaoxybisacetylacetone*, $\text{C}_8\text{H}_{14}\text{O}_5\text{S}_3$, which crystallises from water and melts at 293° .

Trithiotrioxobismethylacetylacetone, $\text{C}_{10}\text{H}_{16}\text{O}_3\text{S}_3$, formed by oxidation of trithiobismethylacetylacetone, separates from alcohol in white crystals and melts at 255° .

Tetrathiotetraoxybisdimethylacetylacetone, $\text{C}_{14}\text{H}_{24}\text{O}_4\text{S}_4$, forms glistening, white crystals and decomposes at about 350° . G. Y.

Fermentation of Sugar without Enzymes. H. SCHADE (*Zeit. physikal. Chem.*, 1906, 57, 1—46).—When an alkaline solution of dextrose is kept at a temperature rather above the ordinary, slow decomposition takes place, and the solution assumes a yellow or brown colour. If hydrogen peroxide has been added to the solution in sufficient quantity, no coloration is observed, even after the lapse of weeks; should there cease to be excess of hydrogen peroxide, the brown colour appears, but it can be destroyed if a little of the peroxide is added immediately after its appearance. It is shown that the brown colour is due to the action of alkali on acetaldehyde, which is produced in the decomposition of the sugar, and the preventive effect of the hydrogen peroxide consists in removing the acetaldehyde

by oxidation to acetic acid. This view is in harmony also with experiments by Framm (Abstr., 1897, i, 5), and others by the author, which show that the production of the brown colour may be prevented also by (1) working under diminished pressure, and so removing the volatile aldehyde, (2) passing a rapid current of oxygen, hydrogen, or nitrogen through the solution, or (3) adding ammonia, sodium hydrogen sulphite, or potassium cyanide—substances which fix the aldehyde.

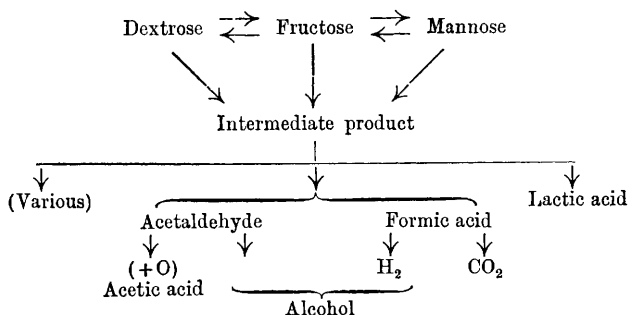
When such means are used to prevent the formation of a brown colour, the two products of the slow decomposition of the sugar (dextrose or lævulose) under the influence of alkali are formic acid and acetaldehyde. Other substances, for example, lactic acid, may be produced, but to an extent which is negligible so far as the main character of the decomposition is concerned.

For every molecule of sugar decomposed, two molecules of formic acid are produced, and it has further been shown, in a less direct manner, that for every molecule of sugar decomposed two molecules of acetaldehyde are produced. Thus the decomposition may be represented by the equation $C_6H_{12}O_6 = 2CH_3 \cdot CHO + 2H \cdot CO_2H$. Galactose and mannose, although but few experiments have been made with them, appear to undergo a similar decomposition. The substances which were found to promote the sugar decomposition in question were potassium and sodium hydroxides, potassium, sodium and lithium carbonates, and disodium hydrogen phosphate. The decomposition is thus a catalysis by the OH' ion, and the velocity of decomposition is proportional to the concentration of that ion.

When a solution of sodium formate, slightly acidified with acetic acid and containing some finely-divided rhodium ("rhodium black") in suspension, is warmed under a reflux condenser, decomposition into carbon dioxide and hydrogen readily takes place. If, however, an amount of acetaldehyde equivalent to the sodium formate is distilled into the sodium formate solution while the latter is being heated, a yield of 60—70 per cent. of ethyl alcohol is obtained. That is, acetaldehyde and formic acid have reacted under the influence of a catalytic agent to form ethyl alcohol and carbon dioxide. Hence ethyl alcohol and carbon dioxide may be obtained from sugars by a purely chemical decomposition, and the change involved in fermentation may be realised without the intervention of enzymes.

The equation $C_6H_{12}O_6 = 2CH_3 \cdot CHO + 2H \cdot CO_2H$ must not be regarded as excluding the possible formation of intermediate products, and in fact it is extremely probable that such are formed. Lactic acid is especially referred to in this connexion, and it is pointed out that, although only traces of this acid were found in the author's experiments, yet when the alkali concentration is high and the solutions are brown in colour considerable quantities are produced. It seems that the decomposition of the sugar (probably through some unknown intermediate product) takes place preferentially into aldehyde and formic acid, but that when this mode of decomposition is checked, possibly through accumulation of the decomposition products, other reactions take place; so, for example, in solutions containing a large quantity of hydroxyl ions, lactic acid is one of the chief products,

The following scheme represents diagrammatically the various possible courses of the sugar decomposition :



A detailed comparison of the purely chemical decomposition of the sugars with the alcoholic fermentation, the lactic acid fermentation, the acetic acid fermentation, and the formic acid fermentation shows that the latter processes are, so far as their end products are concerned, reproducible by agencies of a purely chemical nature. An enzyme is in fact only a catalytic agent of a special kind. J. C. P.

The Liquefaction of Starch Powder and Starch Grains. A. BOLDIN (*Compt. rend.*, 1906, 143, 511—512).—Prior to Fernbach and Wolfe (this vol., i, 804) the author has shown that potassium hydrogen phosphate prevents the liquefaction of starch paste (compare Abstr., 1904, ii, 816), and in the present paper it is shown that whilst magnesium phosphate has a similar action, calcium phosphate does not render starch viscous, and if a solution of purified starch powder is heated in the presence of calcium sulphate or phosphate, it is saccharified to the extent of 33 per cent. Further, if the alkali hydrogen phosphates present in the starch granules are converted into calcium phosphate by the addition of calcium chloride, or into the corresponding di-hydrogen phosphate by the addition of acid, the solution obtained by boiling the starch grains is limpid and mobile and readily saccharified.

M. A. W.

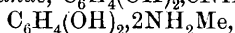
Preparation of Methylamine from Ammonia and Methyl Sulphate. JAMES BURMANN (*Bull. Soc. chim.*, 1906, [iii], 35, 801—803).—Commercial methyl sulphate is added in small portions at a time to excess of a 10 per cent. aqueous solution of ammonia cooled to -5° . The product is then added to excess of a 30 per cent. aqueous solution of sodium hydroxide and the mixture distilled, the issuing gas being passed into hydrochloric acid (20 per cent.). On evaporating, the ammonium chloride separates first and the methylamine hydrochloride ultimately obtained is purified by recrystallisation from boiling absolute alcohol. The yield is about 35 per cent. of the theoretical.

T. A. H.

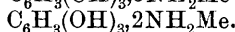
Liquid Methylamine as a Solvent, and a Study of its Chemical Reactivity. HARRY D. GIBBS (*J. Amer. Chem. Soc.*, 1906, 28, 1395—1422).—Liquid methylamine is a very good solvent for

organic compounds, being better than liquid ammonia and probably better than methyl alcohol. For inorganic compounds, however, it is not so good a solvent as liquid ammonia, is far inferior to water, and seems to be approximately equal to methyl alcohol. The solubilities of various organic and inorganic substances have been studied as well as the reactions which sometimes take place.

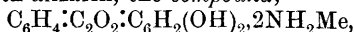
The hydrocarbons are generally very soluble and the solid members crystallise readily from the solutions. The alcohols and phenols are also readily soluble. The following additive compounds are described. The phenol compound, $C_6H_5 \cdot OH, 2NH_2Me$, melts at $8.5-9.0^\circ$. The α -naphthol compound, $C_{10}H_7 \cdot OH, 2NH_2Me$, melts at about 37° . Quinol yields the compounds, $C_6H_4(OH)_2, 8NH_2Me$,



and $C_6H_4(OH)_2, NH_2Me$, the last melting at 105° . Resorcinol gives the compounds, $C_6H_4(OH)_2, 5NH_2Me$, $C_6H_4(OH)_2, 2NH_2Me$, and $C_6H_4(OH)_2, NH_2Me$, the last of which melts at 95° . Pyrogallol furnishes the compounds $C_6H_3(OH)_3, 3NH_2Me$ and

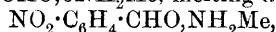


With phenolphthalein, the compound, $C_6H_4 : C_2O_2 : (C_6H_4 \cdot OH)_2, 2NH_2Me$ is obtained, and with alizarin, the compound,



is produced. On evaporating a solution of picric acid in liquid methylamine, a substance is obtained which decomposes without melting at 195° . Thymol yields a crystalline substance melting at 25° .

Acetaldehyde and benzaldehyde are miscible with liquid methylamine. *m*-Nitrobenzaldehyde is readily soluble and gives the compounds, $NO_2 \cdot C_6H_4 \cdot CHO, 6NH_2Me$, melting at -9° , and



which melts and decomposes at 47° .

Acetone, acetophenone, and carbamide dissolve readily in liquid methylamine. Benzil is also very soluble and yields a substance, $COPh \cdot COPh, 2NH_2Me$, which melts at about 23° . Quinone reacts with methylamine with development of heat and formation of a liquid which becomes successively green, purple and black. Anthraquinone is only slightly soluble.

The organic acids are generally very soluble, but in some cases insoluble methylamine salts are produced. The methylamine salts of several organic acids are described. The acetate melts at about 80° , the palmitate at 62° , the succinate at 150° , the tartrate at 148° , the benzoate at $110-112^\circ$, and the *o*-nitrobenzoate at $128-129^\circ$. Phthalic anhydride reacts with methylamine with development of heat and formation of a crystalline substance, which is probably methylamine methylphthalamate, $NHMe \cdot CO \cdot C_6H_4 \cdot CO_2H, NH_2Me$. The urate decomposes without melting.

Chloroform mixes with liquid methylamine in all proportions and slowly reacts with it to form methylcarbimide and methylamine hydrochloride. Ethylene bromide reacts with methylamine with formation of a crystalline substance, which melts at 179° and is probably dimethylethylenediamine hydrobromide. Bromobenzene and *p*-bromoacetanilide dissolve freely without change.

Nitromethane is miscible with liquid methylamine and yields a

crystalline *compound*, $\text{CH}_3 \cdot \text{NO}_2 \cdot \text{NH}_2 \text{Me}$, which melts between -8.0° and -7.5° . Nitrobenzene, *m*-dinitrobenzene, *o*-nitrotoluene, 2:4-dinitrotoluene, and 2:4-dinitroaniline are very soluble. 2:4:6-Trinitroaniline yields a red, crystalline *substance*.

Galactose and dextrose are soluble in liquid methylamine and furnish *compounds* of the composition $\text{C}_6\text{H}_{12}\text{O}_6 \cdot 2\text{NH}_2\text{Me}$. Sucrose is also readily soluble.

Acetamide, phenylhydrazine, amyl formate, pyridine, azobenzene, *m*-nitrobenzenesulphonamide, and benzenesulphonimide are very soluble in liquid methylamine. Diphenylketoxime dissolves readily and yields the *compound*, $\text{CPh}_2 \cdot \text{NOH} \cdot \text{NH}_2\text{Me}$, which decomposes a little below 140° .

Gallein and cœrulein furnish the *compounds* $\text{C}_{20}\text{H}_{12}\text{O}_7 \cdot 3\text{NH}_2\text{Me}$ and $\text{C}_{20}\text{H}_{10}\text{O}_6 \cdot 2\text{NH}_2\text{Me}$. Dichlorogallein and tetrachlorogallein yield products containing about 23 and 25 per cent. of methylamine respectively. Indigotin and rosaniline are readily soluble, whilst methyl orange is only slightly so.

The behaviour of a large number of inorganic salts with liquid methylamine is described. The sulphates are usually insoluble, whilst of the nitrates and haloids some are soluble and others insoluble. The following additive *compounds* are described: $\text{CdI}_2 \cdot 4\text{NH}_2\text{Me}$, $\text{AgNO}_3 \cdot 4\text{NH}_2\text{Me}$, and $\text{AgNO}_3 \cdot 2\text{NH}_2\text{Me}$. Bismuth chloride, calcium chloride, chromic chloride, lithium chloride, lithium nitrate, lead nitrate, mercury methyl chloride, mercuric iodide, and probably cuprous chloride, cupric sulphate, mercurous chloride, and mercuric cyanide also form products containing methylamine of crystallisation.

E. G.

Compounds formed by the Action of Ammonia or Amines on Mercury Salts. DANIEL STRÖMHOLM (*Arkiv Kem. Min. Geol.*, 1906, 2, No. 23, 1–25).—The author classifies the definite compounds formed by ammonia or amines with mercury salts as follows: (A) Those in which $\text{Hg}:\text{X}=1:2$; these are regarded as ammonia compounds. (B) Those in which $\text{Hg}:\text{X}$ is greater than $1:2$, and which are of the types: (1) with ammonia, $\text{NH}_2 \cdot \text{HgX}$, $\text{Hg} \cdot \text{N} \cdot \text{HgX}$, and $\text{Hg} \cdot \text{N} \cdot \text{HgX} + \text{H}_2\text{O}$; (2) with primary amines, $\text{NHR} \cdot \text{HgX}$ and $\text{Hg}(\text{NR} \cdot \text{HgX})_2$. Compounds of the last type have not previously been prepared, although references have been made in the literature to ammonia derivatives of this type; the existence of the latter, however, the author was unable to confirm.

Working under the same conditions as Köhler (*Abstr.*, 1880, 159, and *Ber.*, 1879, 12, 2321), the author was unable to obtain any of the three compounds of ethylamine and mercuric chloride described by this author. Instead, he obtained the *compound* $\text{N}_2\text{Et}_2\text{Hg}_3\text{Cl}_2$ as a white, amorphous mass.

Other compounds prepared from amines are: $\text{NHEt}_2\text{HgCl}_2$, from diethylamine; $\text{N}_2\text{Pr}_2\text{Hg}_3\text{Cl}_2$, from propylamine; $\text{N}_2\text{Me}_2\text{Hg}_3\text{Cl}_2$, from methylamine. Compounds were also obtained from amylamine ($\text{Hg}:\text{Cl}=1.15:1$) and benzylamine ($\text{Hg}:\text{Cl}=0.97:1$).

The interaction of mercuric nitrate, ammonium nitrate, and

ammonia in varying proportions, gave the diammononitrate, aminonitrate, and nitrate of Millon's base, $\text{NHg}_2\cdot\text{OH}$. T. H. P.

Preparation of Amino-alcohols. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 173610).—By the action of ammonia or organic bases on the β -substituted dihalogen hydrins, $\text{OH}\cdot\text{CR}(\text{CH}_2\text{X})_2$, where X is a halogen, new alcohol bases are produced having the general formula $\text{OH}\cdot\text{CR}(\text{CH}_2\cdot\text{NYZ})_2$; these substances or their derivatives are of therapeutic importance owing to their property of dissolving uric acid.

Tetramethyldiaminodimethylethylcarbinol, $\text{OH}\cdot\text{CEt}(\text{CH}_2\cdot\text{NMe}_2)_2$, prepared by heating β -ethyldichlorohydrin with aqueous dimethylamine at 180° , is a limpid oil boiling at 87° under 17 mm. pressure, which can be distilled under the ordinary pressure without decomposition; its *hydrochloride*, $\text{OH}\cdot\text{CEt}(\text{CH}_2\cdot\text{NMe}_2)_2\cdot\text{HCl}$, has a neutral reaction, and is a white, crystalline, hygroscopic substance. The hydriodide is also a well-defined salt.

Diaminodimethylethylcarbinol, $\text{OH}\cdot\text{CEt}(\text{CH}_2\cdot\text{NH}_2)_2$, obtained in a similar manner, boils at 115° under 16 mm. pressure, and is very soluble in water.

Dianilinodimethylethylcarbinol, $\text{OH}\cdot\text{CEt}(\text{CH}_2\cdot\text{NHPh})_2$, prepared by heating β -ethyldibromohydrin and aniline at 200° , is a yellow oil having an odour of quinoline and boiling at $145\text{--}148^\circ$ under 17 mm. pressure.

Tetramethyldiaminophenyldimethylcarbinol, $\text{OH}\cdot\text{CPh}(\text{CH}_2\cdot\text{NMe}_2)_2$, formed by condensing β -phenyldichlorohydrin with aqueous dimethylamine at 180° , is a yellow oil with a basic odour; it boils at $139\cdot5^\circ$ under 11 mm. pressure.

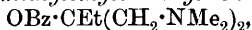
Dipiperidyldimethylethylcarbinol, $\text{OH}\cdot\text{CEt}(\text{CH}_2\cdot\text{C}_6\text{NH}_{10})_2$, is a viscid, colourless oil boiling at 174° under 16 mm. pressure.

Dimethylaminodiethylaminodimethylethylcarbinol,
 $\text{OH}\cdot\text{CEt}(\text{CH}_2\cdot\text{NMe}_2)\cdot\text{CH}_2\cdot\text{NEt}_2$,
 is a colourless liquid boiling at 107° under 16 mm. pressure.

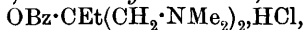
G. T. M.

Preparation of Diaminoalkyl Esters. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 173631. Compare preceding abstract).

—*Tetramethyldiaminodimethylethylcarbinyl benzoate*,



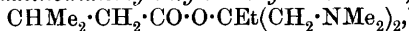
produced by the Schotten-Baumann reaction from tetramethyldiaminodimethylethylcarbinol, forms a *hydrochloride*,



separating in white crystals and melting at 169° .

Tetramethyldiaminophenyldimethylcarbinyl benzoate hydrochloride, $\text{OBz}\cdot\text{CPh}(\text{CH}_2\cdot\text{NMe}_2)_2\cdot\text{HCl}$, produced by benzoylating the corresponding carbinol with benzoyl bromide in pyridine and combining the resulting benzoate with hydrogen chloride (1 mol.), is a white, crystalline powder melting at 187° .

Tetramethyldiaminodimethylethylcarbinyl isovalerate,

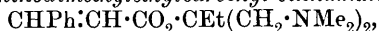


prepared by treating the corresponding carbinol with isovaleryl chloride and sodium hydroxide, is a colourless liquid boiling at 137°

under 16 mm. pressure and having a faint aromatic and basic odour.

Tetramethyldiaminodimethylethylcarbiny ethyl carbonate, obtained from the corresponding carbinol and ethyl chlorocarbonate, is a colourless oil boiling at 129° under 17 mm. pressure; the *hydrochloride* is a white, crystalline powder which melts at 160°.

Tetramethyldiaminodimethylethylcarbiny cinnamate,



is a viscid, colourless oil; its *monohydrochloride* is a white, crystalline powder having a neutral reaction in aqueous solution. This salt produces an anaesthetic effect, lasting twice as long as that brought about by the same quantity of cocaine.

G. T. M.

Copper and Nickel Salts of Certain Amino-acids. ALESSANDRO CALLEGARI (*Gazzetta*, 1906, 36, ii, 63—67. Compare Bruni and Fornara, *Abstr.*, 1904, i, 855; 1905, i, 263; Ley, *Abstr.*, 1905, i, 175).—The *copper* salt of β -aminopropionic acid (β -alanine), prepared by warming the acid with freshly precipitated copper hydroxide, has the properties of an ordinary copper salt and not those of a cuprammonium derivative (*loc. cit.*); the cuprammonium or nickelammonium salts appear to be formed only from α -amino-acids. *Copper aminosulphonate*, $(\text{NH}_2\cdot\text{SO}_2\cdot\text{O})_2\text{Cu}\cdot 2\text{H}_2\text{O}$, prepared by dissolving copper carbonate in an aqueous solution of aminosulphonic acid, forms microscopic, blue crystals and is an ordinary copper salt; the *nickel* salt, $(\text{NH}_2\cdot\text{SO}_3)_2\text{Ni}\cdot 4\text{H}_2\text{O}$, is similar. The copper salt of hydrazinecarboxylic acid (Stollé and Hofmann, *Abstr.*, 1905, i, 28) is apparently a cuprammonium salt, as it has the intense violet colour characteristic of such salts; it cannot be isolated, as it rapidly decomposes, giving metallic copper. The *nickel* salt, $(\text{NH}_2\cdot\text{NH}\cdot\text{CO}_2)_2\text{Ni}$, can be isolated, and is a nickelammonium salt; its solution is intensely blue and does not respond to the usual tests for nickel.

W. A. D.

Optically Active $\alpha\beta$ -Diaminopropionic α - and β -Thioglyceric Acids. CARL NEUBERG and ERICH ASCHER (*Chem. Centr.*, 1906, ii, 1119; from *Biochem. Zeit.*, 1906, 1, 380—382).—The racemic variety of $\alpha\beta$ -diaminopropionic acid can be split into its optically active constituents by the fractional crystallisation of its salt with *d*-camphorsulphonic acid; in this way the dextro-variety can be obtained practically pure. The sulphate of the latter is converted by barium nitrite into *l*-glyceric acid, from which it follows that dextrorotatory $\alpha\beta$ -diaminopropionic acid is in reality a *lævo* form. The *hydrochloride* of *l*-diaminopropionic acid is dextrorotatory; it forms a copper salt, $(\text{C}_3\text{H}_7\text{O}_2\text{N}_2)_2\text{Cu}\cdot\text{H}_2\text{O}$. When protein cystin is treated in sulphuric acid solution with barium nitrite, it is converted into $\alpha\beta$ -thioglyceric acid which has $[\alpha]_D - 10.6^\circ$ (approx.); its *barium* salt, $(\text{C}_3\text{H}_4\text{O}_3\text{S})_2\text{Ba}$, has $[\alpha]_D - 19.08^\circ$. A solution of the barium salt gives heavy precipitates with mercuric chloride, lead, or copper acetates. Zinc and hydrochloric acid reduce the disulphide to β -thioglyceric acid, a substance which, with lead, copper, or iron salts, gives colour reactions similar to those of cystein. In preparing the inactive $\alpha\beta$ -diaminopropionic acid from $\alpha\beta$ -dibromopropionic acid and ammonia, 10 per cent. of the dibromo-acid is

converted into isoserine. Cystin, on dry distillation, loses carbon dioxide, giving *diaminoethylene disulphide*, which was isolated in the form of a picrate. P. H.

Reduction of Oximino-Esters. Synthesis of a New Leucine. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1906, [iii], 35, 965—969).—Most of the facts recorded in this paper have already been given (Abstr., 1905, i, 636).—When ethyl α -oximino- β methylvalerate is reduced with sodium amalgam in a cold alcoholic solution, only 35 per cent. of the theoretical yield of ethyl α -amino- β -methylvalerate is obtained, but a 60 per cent. yield may be secured by effecting the reduction with zinc dust and alcohol saturated with hydrogen chloride. From this amino-ester the corresponding acid (Ehrlich's *isoleucine*, Abstr., 1904, i, 560) may be obtained by agitating its solution in ether with a dilute aqueous solution of sodium hydroxide. The acid yields a *p*-toluenesulphonate which melts at 139°, and when warmed with formic acid (compare Fischer and Warburg, Abstr., 1906, i, 72) furnishes the formyl derivative, $\text{CHMeEt} \cdot \text{CH}(\text{NH} \cdot \text{CHO}) \cdot \text{CO}_2\text{H}$, which crystallises from boiling water and melts at 121—122°. The amino-acid prepared in this way is racemic.

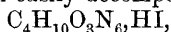
With benzoyl chloride in cooled pyridine solution, ethyl α -aminoisohexanoate forms a *benzoyl* derivative, which crystallises from a mixture of alcohol and light petroleum, melts at 79°, and boils at 211° under 15 mm. pressure. T. A. H.

Additive Compounds of Dicyanodiamide and Inorganic Salts. HERMANN GROSSMANN and BERNHARD SCHÜCK (*Ber.*, 1906, 39, 3591—3593).—The compound $\text{CuSO}_4 \cdot 2\text{C}_2\text{H}_4\text{N}_4 \cdot 4\text{H}_2\text{O}$, formed by heating copper sulphate with dicyanodiamide in aqueous solution on the water-bath, is obtained as a light blue, thick, crystalline precipitate which becomes dark green when dried at 125°; the filtrate yields only green, basic products of varying composition. The compound $\text{CdSO}_4 \cdot 2\text{C}_2\text{H}_4\text{N}_4 \cdot 2\text{H}_2\text{O}$ crystallises in short, colourless prisms, effloresces on exposure to air, and is more soluble in water than is the copper compound. The mercuric compound $\text{HgCl}_2 \cdot \text{C}_2\text{H}_4\text{N}_4$ crystallises in glistening, pointed needles. The copper and cadmium compounds belong to Werner's co-ordinated types $(\text{MA}_6)\text{X}_2$ and $\left(\text{M} \cdot \text{X}_2^{\text{A}_4}\right)$, whilst the mercuric compound is only incompletely co-ordinated. G. Y.

Oxidation of Uric Acid in the presence of Ammonia. GUSTAV DENICKE (*Annalen*, 1906, 349, 269—298).—*Iminoallantoin*, $\text{C}_4\text{H}_7\text{O}_2\text{N}_5$, obtained when finely divided uric acid, suspended in ammonium hydroxide at 0°, is oxidised by one atomic proportion of oxygen derived from potassium permanganate or ferricyanide, separates from hot water in elongated crystals, darkens at 210°, and carbonises at 295° without melting, is soluble in mineral acids, yields oxalic acid with warm potassium hydroxide, and in acid solution or by prolonged boiling with water is converted into allantoin. The resolution into its active components is not effected by tartaric acid.

When the oxidation is performed under similar conditions with

potassium ferricyanide (2 atoms of oxygen), crystals of a *substance*, $C_4H_{10}O_3N_6$, (*A*), are precipitated, whilst from the filtrate a *substance*, $C_4H_8O_2N_6$, (*B*), is obtained; the latter only is formed when the oxidation is effected with more concentrated ammonium hydroxide at the ordinary temperature. The substance *A* darkens at 108° and is carbonised at 295° , dissolves in cold water to an alkaline solution which decomposes by warming, and changes into *B* when digested with ammonium hydroxide. It is soluble in a small quantity of cold concentrated hydrochloric acid (parabanic acid is obtained by warming), and from the solution a *substance*, $C_4H_5O_2N_5$, separates; by saturating the solution with ammonia, oxaluric acid is obtained. With alcoholic hydrogen iodide at -7° , an easily decomposable *hydriodide*,



is formed.

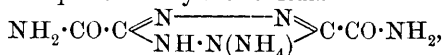
The substance *B* forms microscopic prisms, darkens at 200° , forms a neutral solution in water, and is decomposed by hydrochloric acid, yielding ultimately parabanic acid.

Both *A* and *B* are decomposed by potassium hydroxide, forming urea and a *substance* the composition of which approximates to that of di-iminoparabanic acid, $C_3H_4ON_4$; this substance is a white powder which darkens at 195° , forms a crystalline *potassium* derivative, and by acids is converted into parabanic acid.

The evidence for the formulæ of these substances is discussed.

C. S.

Pseudodiazooacetamide. THEODOR CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1906, **39**, 3410—3437. Compare Curtius, *Abstr.*, 1885, 883; Hantzsch and Silberrad, *Abstr.*, 1900, i, 261; Silberrad, *Trans.*, 1902, **81**, 601).—The ammonium salt of pseudodiazooacetamide is represented by the formula



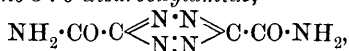
and is most readily prepared by the action of liquid ammonia on ethyl diazoacetate; no diazoacetamide is formed, and only a very small amount of bisdiazooacetamide, which is readily removed. When warmed with water, pseudodiazooacetamide yields one-third of its nitrogen in the gaseous form, one-third as hydrazine, which was estimated as benzylideneazine, and the remainder as glyoxylamide, which was isolated in the form of its phenylhydrazone (Krückeberg, *Abstr.*, 1894, i, 369). Carbon dioxide and oxalic acid do not appear to be formed, although both are produced when pseudodiazooacetamide is boiled with dilute acids.

The *azine* of *glyoxylamide*, $NH_2 \cdot CO \cdot CH : N : N : CH \cdot CO \cdot NH_2$, is obtained as an intermediate product when pseudodiazooacetamide is warmed with water at 60 — 70° in small quantities until nitrogen ceases to be evolved and the solution cooled to 0° . It crystallises in small, pale yellow needles, melts at 202 , is soluble in warm water, but insoluble in alcohol or ether, and is readily hydrolysed, even in the cold, by dilute acids.

Pseudodiazooacetamide is converted into bisdiazooacetamide when

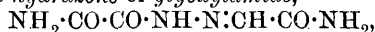
warmed with dilute sodium hydroxide solution, more slowly with the cold alkali, and also when warmed with ammonium hydroxide.

When an aqueous solution containing the ammonium salt of pseudo-diazoacetamide and sodium nitrite is acidified, a bluish-red precipitate of 1:2:4:5-tetrazine-3:6-dicarboxylamide,



is obtained. It is insoluble in all ordinary solvents, and when heated turns brown at 210° and is quite black at 280°. When warmed with water, nitrogen is evolved and the colour disappears. The same amide may be obtained by the oxidation of bisdiazoacetamide with nitric acid; when reduced with hydrogen sulphide, it yields bisdiazoacetamide.

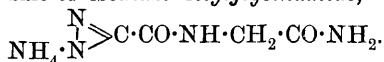
The oxamic acid hydrazone of glyoxyamide,



is obtained when tetrazinedicarboxylamide is boiled with water. It forms a pale yellow, crystalline powder, is insoluble in all ordinary solvents, turns brown at 270°, but is not molten at 300°, and when boiled with dilute sulphuric acid yields semioxamazide (Kerp and Unger, Abstr., 1897, i, 270) together with glyoxylic acid.

The acid previously obtained by Hantzsch and Lehmann (Abstr., 1901, i, 132) and termed bisazoxyacetic acid is now shown to be 1:2:4:5-tetrazine-3:6-dicarboxylic acid. J. J. S.

Action of Ammonia on Ethyl Diazoacetyl glycine. (*iso-Diazoacetyl aminoacetic Acid*). II. THEODOR CURTIUS and JAMES THOMPSON (*Ber.*, 1906, 39, 3398—3409).—The product previously (this vol., i, 404) described as an azomethane derivative is shown to be the ammonium salt of isodiazoacetyl glycineamide,



This ammonium salt is stable, and does not lose ammonia when kept, but is strongly dissociated in aqueous solution; with cold aqueous hydrochloric acid, it gives up 1 mol. of ammonia, and with hot concentrated acid or alkali 2 mols. The ammonium salt reacts with benzoyl chloride and sodium hydrogen carbonate solution, yielding benzoylisodiazoacetyl glycineamide, $\text{N}_2\text{H} : \text{C} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{COPh}$, which crystallises from acetone in slender, colourless needles and melts and decomposes at 185°. The corresponding acetyl derivative, $\text{C}_6\text{H}_8\text{O}_3\text{N}_4$, crystallises from alcohol in colourless needles and melts and decomposes at 158°. When boiled with water or alcohol, it is hydrolysed. The silver salt, $\text{N}_2\text{Ag} : \text{C} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$, obtained by precipitating a solution of the ammonium salt with silver nitrate, forms slender needles, and may be recrystallised from hot water. iso-

Diazoacetyl glycineamide, $\text{N} \begin{smallmatrix} \text{N} \\ | \\ \text{N} \end{smallmatrix} > \text{C} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$, obtained by suspending the silver salt in water, passing in hydrogen sulphide, and evaporating the clear solution under reduced pressure, forms glistening prisms melting and decomposing at 154—155°. It is hygroscopic, and explodes when rapidly heated. It dissolves readily in water, sparingly

in alcohol, and is insoluble in ether, acetone, or chloroform. Its aqueous solution is decidedly acid and decolorises bromine water; when heated with concentrated hydrochloric acid it yields nitrogen (1 mol.) and ammonia (1 mol.). It yields the same benzoyl and acetyl derivatives as are obtained from the ammonium salt. When the ammonium salt is heated with concentrated hydrochloric acid at 130—140° it yields nitrogen, chloroacetic acid, and glycollic acid. When boiled with normal sodium hydroxide solution for an hour, evaporated under reduced pressure, and decomposed at 0° with the theoretical amount of concentrated hydrochloric acid, it yields *isodiazaoacetylaminooacetic acid*, $\text{N}=\text{N} \Rightarrow \text{C} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, in the form of a white, crystalline precipitate, readily soluble in warm water, from which it crystallises in anisotropic, rhombic prisms. The same compound is formed by hydrolysing the ester with sodium hydroxide solution. It possesses both acid and basic properties. The *hydrochloride* forms a crystalline mass melting at 151°. The free acid when slowly heated decomposes at 169—170°.

A considerable amount of potassium cyanide is formed when ammonium *isodiazaoacetyl*glycinamide is fused with potassium hydroxide.

J. J. S.

Remarkable Formation of Alkyl Derivatives of Mercury. JULIUS TAFEL (*Ber.*, 1906, 39, 3626—3631).—Considerable amounts of mercury *sec.*-butyl are formed when methyl ethyl ketone is reduced electrolytically in the presence of mercury cathodes. The maximum yields are obtained at a temperature of 45—50°. The cathode liquid consists of the ketone with some thirteen times its weight of 30 per cent. sulphuric acid, and a voltage of 7.6 to 8.4 for a current of 25 amperes is employed. After some two hours, the amount of crude mercury compound is 1.3 times the weight of ketone used. After several distillations in high vacua, the *mercury sec.-butyl*, $\text{Hg}(\text{C}_4\text{H}_9)_2$, is obtained as a colourless oil boiling at 46° under very low pressures, and a considerable residue of another mercury compound in the form of a yellow oil is left. The mercury butyl boils at 91—93° under 15 mm. pressure, and readily reacts with iodine, yielding *sec.*-butyl iodide and mercury butyl iodide.

J. J. S.

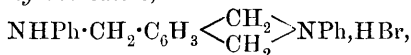
The Study of Hydroaromatic Substances. EDWARD DIVERS, ARTHUR W. CROSSLEY, WILLIAM H. PERKIN, jun., MARTIN O. FORSTER, and HENRY R. LE SUEUR (*Brit. Assoc. Rep.*, 1905, 153).—A report on the production of hydroaromatic substances from the aromatic hydrocarbons, phenols, amines, ketones, and acids. Reference is also made to the nature of double linkings.

G. T. M.

Fluoro-aromatic Compounds. ARNOLD F. HOLLEMAN (*Rec. trav. chim.*, 1906, [ii], 25, 330—333).—*o*- and *p*-Fluoroacetanilides prepared by reducing the crude fluoronitrobenzene (M. Holleman, *Abstr.*, 1905, i, 424) and acetylating the product, can be separated by repeated fractional crystallisation from benzene and light petroleum; *o*-fluoroacetanilide melts at 80°, and *p*-fluoroacetanilide at 150°.

p-Fluorotoluene (Holleman and Beckman, Abstr., 1904, i, 232) freezes in a mixture of solid carbon dioxide and alcohol, whilst the ortho- and meta-isomerides remain liquid. "Fluoro-saccharin" (De Roode, Abstr., 1891, 1226) can be prepared from *p*-fluorotoluene by converting it into *p*-fluorotoluenesulphonic chloride, which boils at 145—150° under 20 mm. pressure and yields the corresponding sulphonamide melting at 140° (De Roode gives 155°) on treatment with ammonium carbonate; this can be oxidised by potassium permanganate to "fluoro-saccharin" melting at 200°. M. A. W.

Action of Bromine on ψ -Cumene. ROBERTO CIUSA (*Gazzetta*, 1906, 36, ii, 90—93. Compare Schramm, Abstr., 1886, 451; Hjelt and Gadd, *ibid.*, 615).—*Tri- ω -bromocumene*, $C_6H_3(CH_2Br)_3$, obtained by adding bromine (3 mols.) to ψ -cumene exposed to direct sunlight, and subsequently heating at 160°, crystallises from light petroleum in white, lustrous needles and melts at 154°. Its structure follows from its yielding with aniline in alcoholic solution 6-anilinomethyl-2-phenyldihydroisindole hydrobromide,



which crystallises from light petroleum and melts at 132°; the base, $C_{21}H_{20}N_2$, also crystallises from light petroleum and melts at 128°.

W. A. D.

Derivatives of *tert*-Butylbenzene. EYVIND BÆDTKER (*Bull. Soc. chim.*, 1906 [iii], 35, 825—836. Compare Abstr., 1904, i, 801).—*p*-Chloro-*tert*-butylbenzene, obtained by condensing chlorobenzene with *tert*-butyl chloride or isobutyl chloride in presence of aluminium chloride, is a limpid liquid with an aromatic odour, boils at 211° (corr.) under 759 mm. pressure, has a sp. gr. 1.0075 at 18.5°/4° and n_D 1.51230 at 20°. On oxidation with chromic acid it furnishes *p*-chlorobenzoic acid. It dissolves in fuming nitric acid, yielding a mixture of 4-chloro-2:3-dinitro-*tert*-butylbenzene and 4-chloro-3:5-dinitro-*tert*-butylbenzene. The first of these is a yellow, crystalline powder and melts at 94—95°, and the second crystallises in hexagonal tablets, large, prismatic needles, or small prismatic grains and melts at 116—117°. When isobutyl chloride is condensed with bromobenzene in presence of aluminium chloride, the principal fraction is a product boiling at 225—226° at atmospheric, or at 110—111° under 15 mm. pressure, and only a small quantity of *p*-bromo-*tert*-butylbenzene is obtained. This boils at 232—233° (compare Schramm, Abstr., 1889, 127). The nature of the fraction boiling at 225—226° has not been definitely ascertained. On oxidation with chromic acid it furnishes *p*-bromobenzoic acid, and on solution in fuming nitric acid yields a mixture of 4-bromo-2:3-dinitro-*tert*-butylbenzene and 4-bromo-3:5-dinitro-*tert*-butylbenzene. The first of these is a yellow, crystalline powder and melts at 92—93°, and the second forms slender, almost colourless, needles and melts at 136°.

p-Iodo-*tert*-butylbenzene, obtained together with di-iodobenzene (Dumreicher, Abstr., 1883, 53) when isobutyl chloride is condensed with iodobenzene in presence of ferric chloride, boils at 253—254°

(corr.) under 766 mm. pressure, has a sp. gr. 1.4392 at 14°/4°, and n_D 1.57076 at 20°, and does not liberate iodine on exposure to light (compare Pahl, Abstr., 1884, 1009, and Bialobrzewski, *ibid.*, 1897, i, 514). On oxidation with chromic acid, it yields *p*-iodobenzoic acid (m. p. 236°; compare Glassner, Abstr., 1875, 888). On nitration, it liberates some iodine and furnishes (a) 4-iodo-2:3-dinitro-*tert*-butylbenzene, which crystallises in lemon-yellow leaflets and melts at 110—111°, and (b) a substance forming colourless prismatic crystals, melting at 243° which may be a di-iodonitrobutylbenzene. When the parent substance is treated with a great excess of fuming nitric acid *p*-iodonitrobenzene is formed.

When *isobutyl* chloride is condensed with cumene in presence of aluminium chloride, *tert*-butylbenzene, *p*-di-*tert*-butylbenzene and propyl chloride are produced. An attempt to separate the constituents of this mixture by Radziewanowski's process (Abstr., 1895, i, 129) gave only a tarry product, which boiled above 300° and decomposed.

When *isoamyl* chloride is condensed with *tert*-butylbenzene in presence of aluminium chloride, *p*-di-*tert*-butylbenzene is produced and the *isoamyl* chloride can be recovered unaltered (compare Baur, Abstr., 1894, i, 445). The hydrocarbon, when dissolved in fuming nitric acid, furnishes 2:6-dinitro-1:4-di-*tert*-butylbenzene, which crystallises from boiling alcohol in slender, colourless needles and melts at 190—191° (corr.). Indications of the presence of an *o*-dinitro-derivative in the mother liquors from the crystallisation of the *m*-dinitro-derivative were obtained.

The dinitro-derivatives obtained from *p*-dibutylbenzene by Verley (Abstr., 1899, i, 424) and Baur (Abstr., 1894, i, 445) are probably impure.

T. A. H.

The Transformation of Aromatic Nitroamines and Allied Substances, and its Relation to Substitution in Benzene Derivatives. FREDERIC S. KIPPING, KENNEDY J. P. ORTON, SIEGFRIED RUHEMANN, ARTHUR LAPWORTH, and JOHN T. HEWITT (*Brit. Assoc. Rep.*, 1905, 103).—A report on the transformation of symmetrically trisubstituted aromatic nitroamines and diazonium hydroxides and on the action of light on solutions of certain diazonium salts.

G. T. M.

Combination of Magnesium Bromide with Certain Amines. VIII. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1906, 38, i, 5).—Aniline reacts with magnesium bromide with development of much heat, giving three compounds. The equilibrium curve of the system magnesium bromide-aniline consists of three branches, representing (1) the solubility of the compound, $MgBr_2 \cdot 6NH_2Ph$ in aniline and ending at 103°; (2) the solubility of the compound $MgBr_2 \cdot 4NH_2Ph$ and ending at 237°; (3) probably the compound $MgBr_2 \cdot 2NH_2Ph$, or $MgBr_2 \cdot NH_2Ph$, but owing to the setting in of decomposition, the investigation could not be carried beyond 250—260°. Phenylhydrazine also gives the compound $MgBr_2 \cdot 6N_2H_3Ph$, and its solubility curve corresponds closely with that of the aniline compound in aniline. The first curve ends at 99°, but owing to decomposition

the second was only observed up to 200°. It probably corresponds with the compound $\text{MgBr}_2 \cdot 4\text{N}_2\text{H}_3\text{Ph}$. Z. K.

Cyanoacetylchloroanilines and the corresponding Oxamic Acids. GALEAZZO PICCININI and A. DELPIANO (*Atti R. Accad. Sci. Torino*, 1906, 41, 1005—1018).—The three chloroanilines react with ethyl cyanoacetate yielding the corresponding chloro-derivatives of cyanoacetylaniline: $\text{NH}_2 \cdot \text{C}_6\text{H}_4\text{Cl} + \text{CN} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} = \text{CN} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Cl} + \text{Et} \cdot \text{OH}$.

m-Chlorocyanoacetylaniline, $\text{C}_9\text{H}_7\text{ONCl}$, prepared from *m*-chloroaniline and ethyl cyanoacetate, crystallises from aqueous alcohol in white, nacreous plates melting at 142° (corr.), dissolves readily in acetone and sparingly in ether or benzene, and is hydrolysed either by dilute alkali solution or, more slowly, by boiling with water.

o-Chlorocyanoacetylaniline crystallises from aqueous alcohol in small, colourless prisms or slender, silky needles melting at 125° and resembles the corresponding meta-compound in its behaviour towards solvents and hydrolytic agents.

p-Chlorocyanoacetylaniline crystallises from aqueous alcohol in shining, colourless prisms which aggregate in the form of plates having a silvery lustre; it melts at 204° and behaves towards solvents and hydrolysis like its isomerides.

When oxidised by means of a large excess of permanganate, these compounds yield, almost quantitatively, the corresponding chlorophenyl-oxamic acids, according to the equation: $\text{C}_6\text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CN} + \text{O}_2 = \text{C}_6\text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{H} + \text{HCN}$.

p-Chlorophenylloxamic acid, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{H}$, crystallises from absolute or aqueous alcohol with 1Et·OH in colourless prisms which melt at 190—191° and effloresce in the air; it dissolves readily in acetone and sparingly in chloroform or benzene. The *potassium, silver, barium, ferric, mercurous, and lead* salts are described.

o-Chlorophenylloxamic acid crystallises with H_2O from aqueous alcohol in colourless, prismatic needles and melts at 93—95°; the anhydrous acid melts at 136—137°. The *potassium, silver, calcium, barium, copper, and mercurous, lead, and ferric* salts are described.

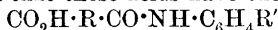
m-Chlorophenylloxamic acid crystallises from water with $1\frac{1}{2}\text{H}_2\text{O}$ in shining needles melting at 90—100°, whilst the anhydrous acid melts at 144—145°; the acid dissolves much more readily than its isomerides in water and is soluble in 95 per cent. alcohol or acetone and sparingly so in benzene or chloroform. The *potassium* salt forms nacreous, anhydrous leaflets.

These three acids exhibit a strong acid reaction in aqueous solution and are monobasic towards alkali hydroxides, using phenolphthalein as indicator. T. H. P.

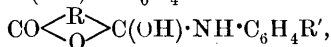
Action of Phenylcarbimide on certain Phenylamic Acids. GINO ABATI and PAOLO GALLO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 291—299).—The authors have examined the behaviour of phenylcarbimide towards solutions, in non-dissociating solvents, of phenylphthalamic, *p*-tolylphthalamic, *d*-*cis*-phenylcamphoramic and *p*-ethoxyphenylmaleinamic acids. With the exception of the phenyl-

camphoramic acid, all the acids are resolved into the corresponding anhydrides and aniline, the latter combining with the phenylcarbimide to form diphenylcarbimide.

This result indicates that these acids have the structure



rather than $\text{CO}_2\text{H}\cdot\text{R}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{R}'$ or

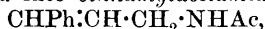


since the last two formulæ contain an alcoholic hydroxyl, which would be capable of reacting with the phenylcarbimide. The non-reactivity of *d-cis*-phenylcamphoramic acid with phenylcarbimide points

to its having the constitution $\begin{array}{c} \text{R}\cdot\text{CO} \\ | \\ \text{C}\cdot\text{O} \end{array} \text{NH}_2\cdot\text{C}_6\text{H}_4\text{R}'$.

In the cases of the above acids which react with phenylcarbimide, a deep yellow substance, readily soluble in ether, is formed in amount too small to allow of its investigation. T. H. P.

Cinnamylamine ("Styrylamine") Bases and their Relation to Ephedrine and ψ -Ephedrine. [ERNST SCHMIDT] and HERMANN EMDE (*Arch. Pharm.*, 1906, 244, 269—299).—Cinnamylamine hydrochloride (E. Schmidt and Flaecher, *Abstr.*, 1905, i, 371) melts at 236°; the *aurichloride* and *mercurichloride* melt at 138—139° and 189° respectively. When the amine is boiled with excess of acetyl chloride it is converted into *cinnamylacetamide*,



which melts at 87.5°. It reacts with methyl iodide in methyl-alcoholic solution at the ordinary temperature; quaternary *cinnamyltrimethylammonium iodide*, melting at 178°, is practically the only product, but much of the amine remains unchanged; the corresponding quaternary *aurichloride* and *platinichloride* melt at 185° and 232—234° respectively.

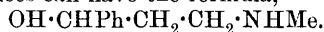
Cinnamyltrimethylamine (*Abstr.*, 1905, i, 370), *aurichloride*, *platinichloride*, *mercurichloride*, $(\text{C}_{12}\text{H}_{18}\text{N})_2\text{HgCl}_4$, $\frac{1}{2}\text{HgCl}_2$, and *picrate* (not analysed) melt at 185°, 228—230°, 171°, and 159° respectively. With methylamine in alcoholic solution at the ordinary temperature cinnamyl chloride in part condenses to form *cinnamylmethylamine hydrochloride*, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NHMe}\cdot\text{HCl}$; this and the corresponding *platinichloride*, *aurichloride*, *mercurichloride*, $\text{C}_{10}\text{H}_{13}\text{N}\cdot\text{HHgCl}_3$, and *picrate* (not analysed) melt at 151.5°, 212°, 103°, 166°, and 147° respectively. When cinnamyl chloride is warmed with pyridine, *cinnamylpyridine hydrochloride*, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_4\cdot\text{HCl}$, is formed; the corresponding *platinichloride*, *aurichloride*, and *picrate* (not analysed) melt at 220—222°, 101.5°, and 146° respectively.

Cinnamyltrimethylamine hydrochloride does not yield additive compounds with hydrogen bromide or iodide in aqueous solution, neither does cinnamylamine hydrochloride take up hydrogen when treated in aqueous alcoholic solution with sodium amalgam. Cinnamyltrimethylamine hydrochloride, however, in aqueous solution is attacked by sodium amalgam: it is decomposed almost quantitatively into α -phenylpropylene, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_3$, and trimethylamine hydrochloride, so that the

reaction can be used advantageously for the preparation of α -phenylpropylene.

Neither cinnamylamine nor cinnamylmethylamine hydrochloride forms a chlorohydrin when treated with hypochlorous acid (aqueous sodium hypochlorite). Cinnamyltrimethylamine hydrochloride does form a *chlorohydrin*, presumably $\text{OH}\cdot\text{CHPh}\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{NMe}_3\text{Cl}$, of which the *platinichloride* and *aurichloride* melt respectively at $210\text{--}212^\circ$ and $130\text{--}132^\circ$; the yield is not quantitative, however. This chlorohydrin is hardly affected by zinc and dilute sulphuric acid, but sodium amalgam does remove the chlorine, forming a quaternary ammonium base, $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_3\cdot\text{OH}$, of which the *aurichloride* and *platinichloride* melt at 103° and $216\text{--}218^\circ$ respectively (a little of this base is formed when cinnamyltrimethylamine chloride is treated with aqueous hydrogen iodide).

As this quaternary base is not identical with either of those prepared by the methylation of ephedrine and ψ -ephedrine respectively, neither of the latter substances can have the formula,

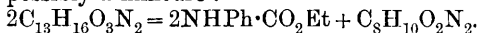


C. F. B.

Condensation of Ethyl Acetoacetate and Phenylcarbamide.

WALTHER KIESSLING (*Annalen*, 1906, **349**, 299—323).—Phenylcarbamide, unlike carbamide, thiocarbamide, or guanidine, condenses with ethyl acetoacetate in the presence of ether, to form not ethyl phenyluraminocrotonate (compare Behrend and Meyer, *Abstr.*, 1901, i, 136), but a yellow oil having the composition $\text{C}_{13}\text{H}_{16}\text{O}_3\text{N}_2$ (compare Behrend, *Abstr.*, 1886, 443), the most suitable temperature being $133\text{--}134^\circ$. The oil, the mean molecular weight of which by the ebullioscopic method is 174.7, is decomposed by cold 5 per cent. hydrochloric acid or by alcohol, giving a yield of ethyl phenylcarbamate in accordance with the equation: $\text{C}_{13}\text{H}_{16}\text{O}_3\text{N}_2 + 2\text{H}_2\text{O} = \text{NHPh}\cdot\text{CO}_2\text{Et} + \text{NH}_3 + \text{CO}_2 + \text{COMe}_2$; the carbamate is also obtained by inoculating the oil at 0° with a crystal of the ester.

For these reasons, the substance is regarded as an easily dissociable compound or possibly a mixture:



The hypothetical substance, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_2$, has not been isolated, but is regarded as containing the skeleton, $\begin{array}{c} \text{MeC}\cdot\text{C}\cdot\text{CO} \\ | \\ \text{MeC}\cdot\text{C}\cdot\text{CO} \end{array}$, since the yellow oil and phenylhydrazine yield Knorr's bisphenylmethylpyrazolone.

Methylcarbamide reacts with ethyl acetoacetate at $125\text{--}127^\circ$ in the presence of ether to form a *substance* which has the composition, but not the properties of ethyl methylaminocrotonate, $\text{C}_7\text{H}_{13}\text{O}_2\text{N}$.

Diphenylcarbamide, ethyl acetoacetate, and ether react at 154° to form a reddish-brown oil (compare Behrend, *Annalen*, 1886, **233**, 11). This substance $\text{C}_{19}\text{H}_{20}\text{O}_3\text{N}_2$ has a mean molecular weight 209, forms bisphenylmethylpyrazolone with phenylhydrazine, and when warmed with hydrochloric acid or alcohol yields ethyl phenylcarbamate. It may be a mixture of ethyl phenylcarbamate and the substance derived from the hypothetical $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_2$, containing 2Ph in the place of hydrogen: $2\text{C}_{19}\text{H}_{20}\text{O}_3\text{N}_2 = 2\text{C}_9\text{H}_{11}\text{O}_2\text{N} + \text{C}_8\text{H}_8\text{Ph}_2\text{O}_2\text{N}_2$.

C. S.

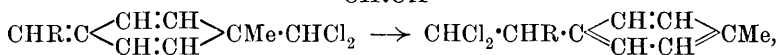
Chlorinated Alcohols [Phenols] of the Dihydrobenzene Series and their Transformation Products. KARL AUWERS (*Ber.*, 1906, **39**, 3748—3757. Compare Auwers and Keil, *Abstr.*, 1903, i, 620; 1904, i, 26; Auwers and Hessenland, *Abstr.*, 1905, i, 434).—The product $C_9H_{12}OCl_2$, obtained with magnesium methyl iodide by Grignard's reaction from 1-keto-2-methyl-2-dichloromethyl-1:2-dihydrobenzene, is an oil which boils at 112—114° under 9 mm. or at 121—122.5° under 13 mm. pressure, and has a sp. gr. 1.202 at 20°/4°, n_D 1.5023 at 19°, and a mol. refraction showing the presence of one double linking. The substance is extremely stable towards dehydrating agents, and is probably an oxide formed by intramolecular change from the tertiary alcohol constituting the product of the Grignard synthesis. When treated with concentrated sulphuric acid, it changes gradually into an *isomeride*, which forms stout crystals, melts at 40—41°, boils at 141—143° under 9 mm. pressure, and has a sp. gr. 1.2254 at 23.5°/4° or 1.2074 at 45°/4°, n_D 1.51419 at 46°, and a mol. refraction pointing to the presence of a ketone with one double linking; the coefficient of dispersion is slightly greater than for the oxide.

The product, $C_{10}H_{14}OCl_2$, formed with magnesium ethyl iodide by Grignard's synthesis from 1-keto-2-methyl-2-dichloromethyl-1:2-dihydrobenzene, is an oil, which boils at 130—131° under 9 mm. pressure, has a sp. gr. 1.1860 at 20°/4° or 1.1833 at 24°/4°, n_D 1.50251 at 20° or 1.50019 at 24°, resembles the methyl derivative in its stability towards dehydrating agents, and yields an oily *isomeride* on treatment with concentrated sulphuric acid.

All the preceding substances are more or less easily attacked by alkali hydroxides, being converted into chlorinated or non-chlorinated unsaturated acids, and finally into unsaturated hydrocarbons.

In the *para*-series, the derivatives of *as-o*-xylenol, *as-m*-xylenol, and ψ -cumenol behave in the same manner as the derivatives of the simpler *para*-substituted phenols.

The labile intermediate products of the series



are *para*-derivatives of alkylidene 1:4-dihydrobenzenes and are isomeric with the final benzene derivatives; these substances, termed by the author "semibenzenes," have mol. refractions higher than the calculated, and abnormally high coefficients of dispersion as compared with the normal dispersions of the aromatic series.

The relation of these facts to the constitution of the semibenzenes is discussed.

G. Y.

Phenyl Chlorothiocarbonates. HENRI RIVIER (*Bull. Soc. chim.*, 1906, [iii], **35**, 837—843).—*Phenyl chlorothioncarbonate*, $CSCl \cdot OPh$, obtained by the action of sodium phenoxide on thiocarbonyl chloride dissolved in chloroform, is a bright yellow liquid with a sharp odour, boils at 91° under 10 mm. and at 100° under 15 mm. pressure, crystallises at -0.5° , and has a sp. gr. 1.283 at 15°/4°. When dissolved in

alcohol it decomposes, slowly in the cold, or immediately at 100° , forming *phenyl ethyl thioncarbonate*, $\text{OEt}\cdot\text{CS}\cdot\text{OPh}$. This is a colourless liquid, with a pleasant ethereal odour, has a sp. gr. $1\cdot135$ at $15^{\circ}/4^{\circ}$, and boils at 124° under 12 mm. and at 130° under 17 mm. pressure. Sodium phenoxide converts phenyl chlorothioncarbonate into diphenyl thioncarbonate, and some of the latter is formed as a by-product in the primary reaction (compare Eckenroth and Kock, Abstr., 1894, i, 408). Phenyl chlorothioncarbonate reacts with thiophenol or, better, with the lead derivative of the latter to form *diphenyl dithiocarbonate*, $\text{SPh}\cdot\text{CS}\cdot\text{OPh}$, which forms golden-yellow prisms and melts at 51° . Ammonia solution in excess decomposes phenyl chlorothioncarbonate, forming phenol and ammonium thiocyanate and chloride, but with smaller quantities *phenyl thioncarbamate*, $\text{NH}_2\cdot\text{CS}\cdot\text{OPh}$, may be obtained. This separates from alcohol in flat, colourless needles and melts at $132\text{--}132\cdot5^{\circ}$. With methylamine, *phenyl methylthioncarbamate*, $\text{NHMe}\cdot\text{CS}\cdot\text{OPh}$, is produced as an oil which could not be obtained pure. With aniline, *phenyl phenylthioncarbamate*, $\text{NHPh}\cdot\text{CS}\cdot\text{OPh}$, is obtained. This crystallises from alcohol in small, colourless needles and decomposes when heated, forming a liquid mixture of phenol and phenylthiocarbimide.

The author agrees with Orndorff and Richmond (Abstr., 1900, i, 156) that the substance described by Dixon (Trans., 1890, 57, 268); Snape (Trans., 1896, 69, 98), and Eckenroth and Kock (*loc. cit.*) as phenyl phenylthioncarbamate was probably thiocarbanilide. *Phenyl dimethylthioncarbamate*, $\text{NMe}_2\cdot\text{CS}\cdot\text{OPh}$, obtained by the action of dimethylamine on phenyl chlorothioncarbonate, separates from ether in colourless prisms and melts at $30\text{--}30\cdot4^{\circ}$. *Phenyl phenylmethylthioncarbamate*, similarly obtained from methylaniline, forms colourless crystals and melts at 104° . Phenyl phenylethylthioncarbamate melts at $69\cdot2^{\circ}$ (compare Billster and Strohl, Abstr., 1888, 364). The last three substances are less readily decomposed by alkalis, water, or alcohol than their analogues described above. T. A. H.

Preparation of 2-Nitro-6-amino-4-acetaminophenol. LEOPOLD CASSELLA & Co. (D.R.-P. 172978). When 4-acetaminophenol is strongly nitrated two nitro-groups are introduced into the ortho-positions with respect to the hydroxyl group. The dinitro-compound when converted into its sodium derivative and reduced by warming with dilute aqueous sodium sulphide, gives rise to 2-nitro-6-amino-4-acetaminophenol, $\text{NHAc}\cdot\text{C}_6\text{H}_2(\text{NO}_2)(\text{NH}_2)\cdot\text{OH}$, which crystallises from alcohol in brownish-red needles and melts at 190° . This substance is feebly basic; its *hydrochloride*, which crystallises in yellow needles, being dissociated by water; with nitrous acid, it yields an orange-yellow *diazo*-derivative. G. T. M.

Preparation of Diaryl Sulphides. FERD. MAUTHNER (*Ber.*, 1906, 39, 3593—3598. Compare this vol., i, 421; Bourgeois, Abstr., 1896, i, 17).—A number of diaryl sulphides, of which those described below are new, have been prepared by the action of aryl iodides on sodium arylmercaptides in presence of copper powder. This reaction constitutes a general method for the preparation of the diaryl sulphides.

o-Tolyl-m-tolyl sulphide, $C_{14}H_{14}S$, from *o*-thiocresol and *m*-iodotoluene, is a colourless, odourless oil, which boils at 170° under 11 mm. pressure. *Di-m-tolyl sulphide*, from *m*-thiocresol and *m*-iodotoluene, is a colourless oil which boils at 174° under 12 mm. pressure.

o-Methoxydiphenyl sulphide, $C_{13}H_{12}OS$, from thiophenol and *o*-iodoanisole, is a colourless oil which has an unpleasant, aromatic odour, and boils at 196° under 11 mm. pressure.

m-Thioanisole, C_7H_8OS , prepared by diazotisation of *m*-anisidine and treatment of the solution with potassium xanthate at $80-90^\circ$, boils at $224-225^\circ$ (corr.). *Di-m-methoxyphenyl sulphide*, $C_{14}H_{14}O_2S$, is a colourless oil which boils at $214-215^\circ$ under 10 mm. pressure.

As the idonitrobenzenes are unstable, the corresponding bromides are employed in the preparation of nitro-derivatives of diphenyl sulphide.

o-Nitrodiphenyl sulphide, $C_{12}H_{11}O_2NS$, crystallises from light petroleum in long, yellow needles, melts at 77° , and gives a green coloration with concentrated sulphuric acid. On reduction with stannous chloride and hydrochloric acid, it yields *o-aminodiphenyl sulphide*, which is obtained as a colourless oil; the *sulphate*, $C_{12}H_{13}O_4NS_2$, forms long needles and is decomposed by water. The *acetyl* derivative, $C_{14}H_{13}ONS$, crystallises in colourless needles and melts at 86° .

o-Nitrophenyl o-tolyl sulphide, $C_{12}H_{11}O_2NS$, from *o*-thiocresol and *o*-bromonitrobenzene, crystallises from light petroleum in yellow needles and melts at $86-87^\circ$, and gives a green coloration with concentrated sulphuric acid.

G. Y.

Aromatic Sulphine Bases. II. FRIEDRICH KEHRMANN and ALFRED DUITENHÖFER (*Ber.*, 1906, **39**, 3559—3560. Compare this vol., i, 83).—Aryldimethylsulphine salts are formed by heating the aromatic mercaptans with an excess of methyl sulphate at 100° ; the methyl mercaptide formed in the first stage of the reaction combines with methyl sulphate, forming the aryldimethylsulphine methyl sulphate, $SRMe_2 \cdot O \cdot SO_3Me$. The corresponding aryldiethylsulphine salts are formed in the same manner but less readily.

Phenyldimethylsulphine platinichloride, $(C_8H_{11}S)_2PtCl_6$, forms orange, yellow crystals, melts and decomposes at $165-166^\circ$, and is slightly soluble in water.

α -Naphthyldimethylsulphine platinichloride, $(C_{12}H_{13}S)_2PtCl_6$, is obtained as a sandy, crystalline, flesh-coloured precipitate, which melts and decomposes at 174° . *β -Naphthyldimethylsulphine platinichloride* forms a flesh-coloured, crystalline powder, and melts and decomposes at 177° .

G. Y.

Preparation of Aminonaphthols. FRANZ SACHS (D.R.-P. 173522. Compare this vol., i, 829).—The sulphonic group of a naphtholsulphonic acid may be replaced with great facility by an amino-group when the acid is heated with sodamide at high temperatures, especially in the absence of air, or in the presence of inert diluting materials such as naphthalene or quinoline. β -Naphthol-7-sulphonic acid furnished 2-amino- β -naphthol, whilst α -naphthol-5-sulphonic acid gave rise to 5-amino- α -naphthol. These products were characterised by their dibenzoyl derivatives.

In some cases isomeric change occurred; thus β -naphthol-6-sulphonic

acid gave a good yield of 5-amino- β -naphthol and β -naphthol-8-sulphonic acid furnished a mixture of 5-amino- β -naphthol and other isomerides.

G. T. M.

Resolution of Aminobenzyl- β -naphthol into its Optical Antipodes. MARIO BETTI (*Gazzetta*, 1906, 36, ii, 392—394. Compare Abstr., 1901, i, 611).—Racemic aminobenzyl- β -naphthol (aminobenzylidene- β -naphthol) can be readily separated into its constituents by adding an alcoholic solution of tartaric acid to a solution of the compound in 95 per cent. alcohol; in the course of twelve hours, the liquid deposits the *d*-amine-*d*-tartrate in almost theoretical amount. This tartrate forms small, shining crystals and begins to soften and turn yellow at about 180° and decomposes above 240°.

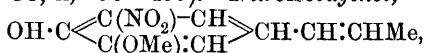
d-Aminobenzyl- β -naphthol, $\text{NH}_2 \cdot \text{CHPh} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$, crystallises from ether in white, silky needles, melts at 137°, and in benzene solution has $[\alpha]_D + 58.84^\circ$ at 18°. Its *hydrochloride* has $[\alpha]_D + 52.89^\circ$ in alcoholic solution at 18°.

l-Aminobenzyl- β -naphthol melts at 136—137°, and has $[\alpha]_D - 58.96^\circ$. Its *hydrochloride* has $[\alpha]_D - 52.51^\circ$.

It is noteworthy that the racemic compound melts at a lower temperature (124°) than its constituent isomerides, this being very seldom the case.

T. H. P.

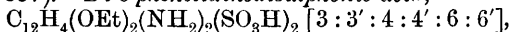
Nitroisoeugenol. ERNESTO PUXEDDU and MATTEO COMELLA (*Gazzetta*, 1906, 36, ii, 450—455).—*Nitroisoeugenol*,



prepared by the action of nitric acid on *isoeugenol* in acetic acid solution, separates from amyl or *isobutyl* alcohol in a reddish-yellow, amorphous mass decomposing at about 150°, and is readily soluble in alcohol or chloroform; it dissolves in concentrated nitric acid, giving a reddish-brown coloration, and in concentrated sulphuric acid forming an intensely brown solution; it is very readily soluble in dilute alkali solution, yielding a blood-red liquid with a peculiar odour. Its *bromo*-derivative, $\text{C}_7\text{H}_7\text{O}_4\text{N} \cdot \text{CBr} : \text{CHMe}$ or $\text{C}_7\text{H}_7\text{O}_4\text{N} \cdot \text{CH} : \text{CBrMe}$, separates from alcohol as a reddish-yellow, amorphous powder, and begins to decompose at 175°; it dissolves in amyl alcohol, acetic acid, concentrated nitric or sulphuric acid or dilute alkali solution, and, to a slight extent, in ether or light petroleum. Its *acetyl* derivative, $\text{C}_{12}\text{H}_{13}\text{O}_5\text{N}$, is deposited from alcohol as a yellowish-brown, amorphous powder decomposing above 200°.

T. H. P.

Preparation of a Di-*o*-phenetidinedisulphonic Acid. AKTIEN GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 174497. Compare this vol., i, 837).—*Di-o-phenetidinedisulphonic acid*,



is readily produced by treating *di-o-phenetidine* with fuming sulphuric acid at moderately low temperatures; it is readily soluble in water, whereas its sodium salt dissolves only sparingly and crystallises from water in lustrous leaflets.

G. T. M.

Preparation of 4-Alkyloxy- α -naphthols. BADISCHE ANILIN-UND SODA-FABRIK (D.R.-P. 173730).—Generally the two hydroxyl groups of the dihydroxynaphthalenes are alkylated with equal readiness, so that the dialkyloxynaphthalenes are produced, but it now found that 1:4-dihydroxynaphthalene readily undergoes monoalkylation when the etherification process is discontinued so soon as the dihydroxy-compound has disappeared.

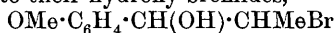
4-Methoxy- α -naphthol, $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, is prepared by dissolving 1:4-dihydroxynaphthalene in cold methyl-alcoholic hydrochloric acid and leaving the solution at the ordinary temperature for fifteen hours. When crystallised from light petroleum or benzene, the ether separates in colourless needles and melts at 131° (Abstr., 1900, i, 601).

4-Ethoxy- α -naphthol, produced by heating 1:4-dihydroxynaphthalene with alcoholic hydrochloric acid for thirty minutes, crystallises in colourless needles and melts at $104\text{--}105^\circ$ (*loc. cit.*).

4-isoAmyloxy- α -naphthol forms colourless needles and melts at 98° .

G. T. M.

Preparation of Anethole and isoSafrole Oxides. PAUL HÖRING (D.R.-P. 174496).—The dibromides of anethole and isosafrole when warmed with granulated marble in moist acetone solution are readily converted into their hydroxy-bromides,



and $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}(\text{OH})\cdot\text{CHMeBr}$. These substances or their acetyl derivatives when warmed with alcoholic sodium hydroxide or ethoxide lose another molecule of hydrogen bromide and become transformed into the corresponding oxides.

Anethole oxide, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\begin{smallmatrix} \text{CHMe} \\ \diagup \text{O} \end{smallmatrix}$, is an oil boiling at 132° under 11 mm. pressure and having a sp. gr. 1.0637 at 17° . When warmed at $190\text{--}210^\circ$ under ordinary pressure, the oxide undergoes isomeric change into the ketone, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{COMe}$, which boils at $267\text{--}269^\circ$ under ordinary pressure and at $136\text{--}138^\circ$ under 12 mm. pressure and has a sp. gr. 1.0707 at 17° .

isoSafrole oxide, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\begin{smallmatrix} \text{CHMe} \\ \diagup \text{O} \end{smallmatrix}$, is a colourless oil having a more pleasant odour than the preceding oxide; it boils at $149\text{--}151^\circ$ under 12 mm. pressure and has a sp. gr. 1.2128 at 17° . At $200\text{--}220^\circ$ this oxide is transformed with development of heat into the isomeric ketone, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{COMe}$; this boils at $149\text{--}151^\circ$ under 11 mm. or at $283\text{--}284^\circ$ under the ordinary pressure, and has the sp. gr. 1.2017 at 17° .

G. T. M.

Amount of Cholesterol in Fats and Mineral Oils and their Probable Genetic Relationships. M. A. RAKUSIN (*Chem. Zeit.*, 1906, 30, 1041—1042).—The presence of cholesterol in a number of oils of animal, vegetable, and mineral origin has been shown both by means of the colour reactions described by Tschugaeff, which consist in heating the substance with acetyl chloride in the presence of zinc chloride or with trichloroacetic acid, and by measurement of the optical rotation. The presence of cholesterol in mineral oils is

regarded as a clear proof of their origin from animal and vegetable sources; the low optical activity of some of the American oils is attributed to their containing the racemic modification of cholesterol.

P. H.

Colour Phenomena Connected with Liquid Crystals. [Cholesterol Compounds]. OTTO LEHMANN (*Chem. Centr.*, 1906, ii, 858; from *Physikal. Zeit.*, 7, 578—584).—An account of the play of colours observed when cholesteryl acetate propionate, isobutyrate, *n*-valerate, isovalerate, decoate, or octoate are examined between crossed nicols. When fused cholesteryl decoate is slowly cooled, it passes through two modifications of liquid crystals. In the first form the crystals are very small and mobile, and exhibit feeble double refraction; in the second form the crystals are larger and less mobile, but their double refraction is greater. The colour phenomena exhibited by mixtures of the decoate or the benzoate with *p*-azoxyphenetole are also described.

P. H.

Solubility of Certain Benzoates in Water: Strontium Benzoate. RAFFAELLO PAJETTA (*Gazzetta*, 1906, 36, iii, 67—70).—The solubility of strontium benzoate is as follows in grams of anhydrous salt per 100 grams of solution: at 15.7°, 5.31; at 24.7°, 5.40; at 31.4°, 5.40; at 40.9°, 5.77. Of potassium benzoate (expressed similarly) at 17.5°, 41.1; at 25.0°, 42.4; at 33.3°, 44.0; at 50.0°, 46.6. Of normal lead benzoate, at 18°, 0.149; at 40.6°, 0.249; at 49.5°, 0.310. The solubility of zinc benzoate diminishes with rise of temperature: at 15.9°, 2.55; at 17.0°, 2.49; at 27.8°, 2.14; at 31.3°, 2.05; at 37.5°, 1.87; at 49.8°, 1.62; at 58.0°, 1.45.

W. A. D.

Preparation of Benzoylalkylaminoethanols [Alkylaminoethyl Benzoates]. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 175080).—By benzoylating the alkylaminoethanols or their salts, benzoyl derivatives are obtained which have valuable anæsthetic properties.

Diethylaminoethyl benzoate, $\text{NEt}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OBz}$, obtained by treating diethylaminoethanol with benzoic anhydride in aqueous solution is a viscid oil; its hydrochloride separates from a mixture of alcohol and ether in long needles melting at 124—125°. This salt is much more soluble in water than the hydrochlorides of the known synthetical local anæsthetics: "holocaine," "eucaine," &c., and is much less toxic than "stovaine" (dimethylaminodimethylethylcarbinyll benzoate hydrochloride).

Dimethylaminoethyl benzoate, $\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OBz}$, is a viscid oil; its hydrochloride readily dissolves in water or alcohol, but not in ether, crystallises in white leaflets, and melts at 136—137°.

Methylaminoethyl benzoate is an oil which forms a hydrochloride, crystallising in lustrous leaflets and melting at 108—109°.

Diisooamylaminoethyl benzoate crystallises from a mixture of ethyl acetate and light petroleum and melts at 87—88°; its oxalate crystallises from water in spherical aggregates of sparingly soluble needles and melts at 152—153°.

G. T. M.

Reversible Reactions among Derivatives of Organic Acids. JOACHIM BIEHRINGER and WILHELM BORSUM (*Ber.*, 1906, 39, 3348—3356).—The qualitative conditions are discussed under which a number of simple organic reactions become reversible. Thus, in sealed tubes at 150°, benzoic acid and acetyl chloride form benzoyl chloride and acetic acid, but at 120°, under ordinary pressure, change proceeds in the contrary direction. Whereas the interaction of benzoic acid and acetamide takes place in one direction only, ethyl acetate and benzamide yield acetamide and ethyl benzoate when heated for six hours under pressure at 260°, whilst the reverse change takes place on heating under pressure from 270° to 290°. Phenyl benzoate and ammonia interact in sealed tubes at 150°, whilst benzamide and phenol yield phenyl benzoate when heated. Other cases considered are the interaction of oxalic acid and acetamide, of benzoic acid and acetanilide, and of acetanilide and benzoyl chloride. Diacetyl-*o*-tolidine and *o*-tolidine when heated together in sealed tubes at 240° give rise to *monoacetyl-o-tolidine*, forming pale yellow crystals which melt at 133—135°, rapidly become green when exposed to the atmosphere, and decompose when moist at 100°. E. F. A.

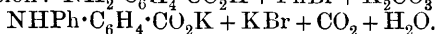
Formation and Behaviour of Thiobenzanilide. ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 379—384).—The author has prepared thiobenzanilide by the action of phosphorus pentasulphide on benzophenoneoxime and, after crystallising from alcohol and light petroleum, dissolving in dilute potassium hydroxide solution and precipitating by means of carbon dioxide and again crystallising from light petroleum, it melted at 96°. When dissolved in potassium hydroxide solution and boiled with silver nitrate, it is converted into benzanilide.

With silver nitrate, thiobenzanilide forms a *salt*, $(C_{13}H_{11}NS)_2, AgNO_3$, which separates in long, yellow needles, deflagrates and melts at 115°, and is soluble in chloroform, ethyl acetate, or methyl alcohol.

When reduced by means of zinc dust and potassium hydroxide solution, thiobenzanilide gives a yellow oil, which yields benzaldehyde on boiling with hydrochloric acid. As the thioanilides are easily obtained, this reaction affords a ready means of passing from an acid to the corresponding aldehyde. T. H. P.

Preparation of Arylanthranilic Acids. IRMA GOLDBERG and FRITZ ULLMANN (D.R.-P. 173523).—Arylanthranilic acids are obtained when anthranilic acid is treated with aromatic bromo-derivatives in the presence of copper as a catalyst.

Phenylanthranilic acid is produced in a state of purity by heating to boiling a mixture of anthranilic acid, potassium carbonate, bromobenzene, and amyl alcohol to which a small amount of cuprous chloride has been added. The reaction takes place in accordance with the following equation: $NH_2 \cdot C_6H_4 \cdot CO_2H + PhBr + K_2CO_3 =$

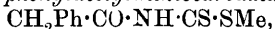


By replacing bromobenzene by other brominated benzene derivatives, similar arylanthranilic acids are prepared; *p*-bromonitrobenzene gives rise to 4-nitrophenylanthranilic acid, $NO_2 \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot CO_2H$, which

crystallises in yellow needles and melts at 211° . The use of *p*-dibromobenzene leads to the formation of *p*-phenylenebis-*o*-aminobenzoic acid, $C_6H_4(NH \cdot C_6H_4 \cdot CO_2H)_2$, which melts at 288° ; it is very sparingly soluble in the ordinary organic media, but dissolves in boiling nitrobenzene.
G. T. M.

Thiocyanates and Thiocarbimides. VI. TREAT B. JOHNSON (*J. Amer. Chem. Soc.*, 1906, 28, 1454—1461. Compare Wheeler and Johnson, *Abstr.*, 1902, i, 760).—Phenylthioacetic, *m*- and *p*-bromothiobenzoic, and *m*-nitrothiobenzoic acids have been prepared by dissolving the corresponding acyl chlorides in a solution of potassium hydrogen sulphide and treating the resulting potassium salts with hydrochloric or sulphuric acid. These thiol acids react smoothly with methyl, ethyl, and benzyl thiocyanates with formation of the corresponding dithiocarbamates. Phenylthioacetic, *p*-bromothiobenzoic, and *m*-nitrothiobenzoic acids react quantitatively with phenylthiocarbimide with production of the corresponding acylanilines.

[With ERNEST BATEMAN, ERIK S. PALMER, and CHARLES A. BRAUTLECHT].—Phenylthioacetic acid, $CH_2Ph \cdot CO \cdot SH$, is obtained as a limpid oil, and when left in the air is slowly converted into the disulphide. Diphenylacetyl disulphide, $(CH_2Ph \cdot CO)_2S_2$, prepared by suspending finely powdered iodine in an aqueous solution of sodium phenylthioacetate, crystallises from alcohol in transparent plates and melts at 62° . Methyl phenylacetyldithiocarbamate,

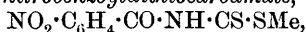


crystallises in slender prisms and melts at 133° . The corresponding ethyl ester separates from alcohol in lemon-yellow prisms and melts at 125° .

m-Bromothiobenzoic acid, $C_6H_4Br \cdot CO \cdot SH$, separates from light petroleum as a pale yellow, crystalline powder, melts at 58° , and is very soluble in alcohol, ether, or benzene. Methyl-*m*-bromobenzoyldithiocarbamate, $C_6H_4Br \cdot CO \cdot NH \cdot CS \cdot SMe$, crystallises in needles and melts at 124° ; the corresponding ethyl and benzyl esters crystallise in prisms and melt at 131° and 113° respectively.

p-Bromothiobenzoic acid, $C_6H_4Br \cdot CO \cdot SH$, crystallises from hot alcohol in prisms and melts at 78 — 79° . *p*-Bromobenzoylaniline melts at 201 — 202° instead of at 197° as stated by Raveill (*Abstr.*, 1884, 600). Methyl *p*-bromobenzoyldithiocarbamate, $C_6H_4Br \cdot CO \cdot NH \cdot CS \cdot SMe$, crystallises in needles and melts at 152° ; the corresponding ethyl ester forms pale yellow needles and melts at 116° .

m-Nitrothiobenzoic acid, $NO_2 \cdot C_6H_4 \cdot CO \cdot SH$, forms light yellow, prismatic crystals and melts at 89 — 90° ; the sodium salt is very soluble in water. Methyl *m*-nitrobenzoyldithiocarbamate,



crystallises from benzene in yellow needles, melts at 162° , and is very soluble in benzene and sparingly so in alcohol; the corresponding ethyl ester separates from hot alcohol in yellow prisms and melts at 158° .
E. G.

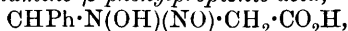
Unsaturated Compounds. II. The Addition of Free Hydroxylamine to Cinnamic Acid. Constitution and Derivatives of β -Hydroxylamino- β -phenylpropionic Acid. THEODOR POSNER (*Ber.*, 1906, 39, 3515—3529. Compare *Abstr.*, 1904, i, 160).—The substance produced by the direct addition of hydroxylamine to cinnamic acid was formerly regarded as being α -hydroxylamino- β -phenylpropionic acid, because on reduction it yielded the compound which was then considered to be α -aminodihydrocinnamic acid. The latter has since been shown to be β -amino β -dihydrocinnamic acid (*Abstr.*, 1905, i, 577), and consequently the original additive compound is β -hydroxylamino- β -phenylpropionic acid. $\text{OH}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, melting at 166° . *Diacetyl* and *dibenzoyl- β -hydroxylamino- β -phenylpropionic acids* form colourless crystals melting respectively at 166 — 167° and 110° .

On oxidation with ammoniacal silver nitrate, the hydroxylamino-acid furnishes 3-phenylisooxazolone, the *nitroso*-derivative of which melts at 143° .

Acetyl-3-phenylisooxazolone, $\text{NAc} < \begin{smallmatrix} \text{CPh}\cdot\text{CH} \\ \text{O} \text{---} \text{CO} \end{smallmatrix}$, forms white needles melting at 137 — 138° ; it is readily soluble in aqueous ammonia and alkalis, and is reprecipitated by dilute acids.

Bromo-3-phenylisooxazolone, $\text{C}_9\text{H}_6\text{O}_2\text{NBr}$, produced by brominating 3-phenylisooxazolone in chloroform solution, separates from methyl alcohol in prismatic crystals and melts at 121 — 122° . β -Hydroxylamino- β -phenylpropionic acid is very readily alkylated by treatment with a mixture of the appropriate alcohol and concentrated hydrochloric acid on the water-bath. *β -Methoxylamino- β -phenylpropionic acid* and the *ethoxyl* compound crystallise in colourless needles and melt respectively at $101\cdot5$ — $102\cdot5^\circ$ and $74\cdot5$ — 75° . Both alkyl derivatives are readily hydrolysed by alkalis, although fairly stable to cold dilute acids. They both furnish, on oxidation with ammoniacal silver nitrate, good yields of 3-phenylisooxazolone.

β -Nitrosohydroxylamino- β -phenylpropionic acid,



is a very unstable compound obtained by the action of nitrous acid on β -hydroxylamino- β -phenylpropionic acid or its alkyl derivatives; when quickly prepared and isolated, it forms a colourless, crystalline powder melting at 133° . On heating or even on dissolving it in warm benzene, it evolves nitrous fumes and changes into *2-hydroxy-3-phenylisooxazolidone*, $\text{OH}\cdot\text{N} < \begin{smallmatrix} \text{CHPh}\cdot\text{CH}_2 \\ \text{O} \text{---} \text{CO} \end{smallmatrix}$, a pale yellow, crystalline powder easily soluble in methyl or ethyl alcohol, and dissolving readily in aqueous alkalis, but not in dilute acids.

2-Methoxy-3-phenylisooxazolidone, $\text{OMe}\cdot\text{N} < \begin{smallmatrix} \text{CHPh}\cdot\text{CH}_2 \\ \text{O} \text{---} \text{CO} \end{smallmatrix}$, is obtained

either by the action of methyl sulphate on the foregoing compound, or by the decomposition in benzene solution of the nitroso-compound of β -methoxylamino- β -phenylpropionic acid; it crystallises from benzene in rectangular prisms and melts at 128° .

2-Ethoxy-3-phenylisooxazolidone melts at 109°, and, like the foregoing methyl compound, is insoluble in aqueous alkalis.

On attempting to acetylate 2-hydroxy-3-phenylisooxazolidone with acetic anhydride, a crystalline product was obtained which was decomposed by sodium carbonate into an acidic and a neutral part. The acidic compound has a composition approximating to $C_{18}H_{14}O_6$, the neutral substance corresponds with the formula $C_{22}H_{18}O_4$. G. T. M.

Condensation of Acetylenic Nitriles with Amines. General Method of Synthesis of β -Substituted Derivatives of β -Amino-substituted Acrylonitriles. CHARLES MOUREU and I. LAZENNEC (*Compt. rend.*, 1906, 143, 553—555. Compare this vol., i, 148, 240, 276, 432).—Phenylpropionitrile unites directly with piperidine to form β -piperidyl- β -phenylacrylonitrile, $C_5NH_{10} \cdot CPh:CH:CN$, which is a neutral substance melting at 92°, stable towards alkalis, but readily hydrolysed by hydrochloric, picric, or oxalic acid with the regeneration of piperidine and formation of cyanoacetophenone, according to the equations: $C_5NH_{10} \cdot CPh:CH:CN + H_2O = C_5NH_{11} + [OH \cdot CPh:CH:CN] \rightarrow CPh:CH_2:CN$.

This reaction between acetylenic nitriles and primary or secondary amines is a general one, and the following compounds were thus prepared: β -Benzylamino- β -amylacrylonitrile,

$CH_2Ph \cdot NH \cdot C(C_5H_{11}):CH:CN$,
melting at 64—65°; β -piperidyl- β -amylacrylonitrile,
 $C_5NH_{10} \cdot C(C_5H_{11}):CH:CN$,

boiling at 218—219° (corr.) under 23 mm. pressure, and having a sp. gr. 0.950 at 24°; β -benzylamino- β -hexylacrylonitrile,

$CH_2Ph \cdot NH \cdot C(C_6H_{13}):CH:CN$,
melting at 48°; β -piperidyl- β -hexylacrylonitrile,
 $C_5NH_{10} \cdot C(C_6H_{13}):CH:CN$,

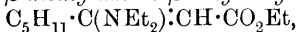
boiling at 236—238° (corr.) under 27 mm. pressure and having a sp. gr. 0.943 at 24°; β -benzylamino- β -phenylacrylonitrile,

$CH_2Ph \cdot NH \cdot CPh:CH:CN$,
melting at 86°; β -diethylamino- β -phenylacrylonitrile, $NEt_2 \cdot CPh:CH:CN$,
melting at 70°; and β -piperidyl- β -phenylacrylonitrile, melting at 92°.

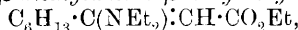
M. A. W.

Condensation Products of Acetylenic Esters and Amines. CHARLES MOUREU and I. LAZENNEC (*Compt. rend.*, 1906, 143, 596—598. Compare preceding abstract).—The acetylenic esters readily condense with primary and secondary amines to form the amino-substituted derivative of the corresponding ethylene ester, and these compounds do not form salts with acids as stated by Ruhemann and Cunningham (*Trans.*, 1899, 75, 954), but are hydrolysed with regeneration of the base and formation of the corresponding β -ketonic ester. Thus, ethyl phenylpropionate condenses with diethylamine to form ethyl β -diethylamino- β -phenylacrylate, $NEt_2 \cdot CPh:CH:CO_2Et$, which is readily hydrolysed in the cold by acids yielding the corresponding salt of diethylamine and ethyl benzoylacetate. The hydrolysis is effected by passing hydrogen chloride into an ethereal solution of the compound or by adding to the solution an equivalent quantity of picric or

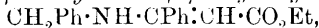
oxalic acid dissolved in ether and alcohol. The following compounds were obtained: *ethyl β-diethylamino-β-amyloxyacrylate*,



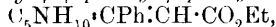
boiling at 170—178° under 26 mm. pressure and having a sp. gr. 0.9316 at 24°; *ethyl β-diethylamino-β-hexyloxyacrylate*,



boiling at 185—195° under 24 mm. pressure, and having a sp. gr. 0.9211 at 24°; *ethyl β-benzylamino-β-phenyloxyacrylate*,



melting at 72°; and *ethyl β-piperidyl-β-phenyloxyacrylate*,



boiling at 225—228° (corr.) under 23 mm. pressure, and having a sp. gr. 1.072 at 24°.

M. A. W.

Preparation of Hydroxyethyl Salicylate. BADISCHE ANILIN-UND SODA-FABRIK (D.R.-P. 173776).—*β-Hydroxyethyl salicylate*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, the hitherto unknown monosalicylate of ethylene glycol, is readily prepared by the interaction of the metallic salicylates and the ethylene halogen hydrins; thus on heating at 140—150° for several hours a mixture of sodium salicylate and ethylene chlorohydrin, and extracting the product successively with water and ether, the ester is obtained as solid melting at 37°, and boiling at 169—170° under 12 mm. pressure. With ferric chloride it develops a violet coloration.

G. T. M.

Reductions with Phenylhydrazine. I. New Method of Preparing 5-Aminosalicylic Acid. ERNESTO PUXEDDU (*Gazzetta*, 1906, 36, ii, 87—89. Compare Abstr., 1905, i, 842).—5-Aminosalicylic acid, $[\text{CO}_2\text{H}:\text{OH}:\text{NH}_2=1:2:5]$, is easily prepared by warming 5-nitrosalicylic acid with phenylhydrazine; action begins at slightly above 100° and proceeds rapidly. The yield is good.

W. A. D.

Constitution of the Aromatic Purpuric Acids. IX. Behaviour on Oxidation with Potassium Hypobromite. WALTHER BORSCHKE and G. GAHRTZ (*Ber.*, 1906, 39, 3359—3366. Compare Abstr., 1905, i, 894).—Potassium *m*-purpurate when oxidised with potassium hypobromite yields 2:6-dinitro-3-hydroxybenzonitrile of which the *aniline* derivative crystallises in golden-yellow needles melting at 162—163°, and the *acetate* forms yellow, glistening platelets melting at 122—123°. Potassium *o*-tolylpurpurate under similar treatment yields 2:6-dinitro-3-hydroxy-4-toluenitrile. 4-Bromo-2:6-dinitro-3-hydroxybenzonitrile, obtained on oxidising potassium bromo-*m*-purpurate, crystallises in yellow needles melting at 152°, the *aniline* salt forms canary-yellow needles melting at 185°, whilst 4-bromo-2:6-dinitro-3-hydroxybenzamide separates from water in glistening, yellowish-white plates melting at 231°. Potassium naphthylpurpurate gives rise to 2:4-dinitro-1-hydroxy-3-naphthonitrile, crystallising in bright yellow, glistening needles which melt at 165—166°: the *aniline* salt is a yellow, crystalline powder melting at 152°.

Cyanopicric acid (2:4:6-trinitro-3-hydroxybenzonitrile), prepared

by nitration of dinitrohydroxybenzonitrile, crystallises in yellowish-white needles or plates and melts at 131—132°: the *aniline* salt forms yellow needles which melt at 179—180°. E. F. A.

Conversion of Racemic Compounds into Optically Active Compounds. WILLY MARCKWALD and DAVID M. PAUL (*Ber.*, 1906, 39, 3654—3655. Compare *Abstr.*, 1905, i, 285).—When *l*-mandelic acid is heated with an equivalent quantity of brucine for twenty hours at 150—160° and the acid recovered, it is found to be dextrorotatory with $[\alpha]_D + 0.45^\circ$ to $+ 0.6^\circ$. When *r*-mandelic acid is heated with other alkaloids, the recovered acid is found to be dextrorotatory, but the amount of rotation varies with the alkaloid employed. With strychnine the recovered acid has $[\alpha]_D + 2.05^\circ$ and with nicotine $+ 0.4^\circ$.

r-*p*-Methoxymandelic acid has $[\alpha]_D + 1.2^\circ$ to $+ 1.5^\circ$, when heated with brucine or strychnine, and β -phenyllactic acid has $[\alpha]_D - 0.16^\circ$ when heated with brucine for five hours at 150—160°.

α -Methylbutyric acid, and β -phenyl- α -methylpropionic acid are not affected when heated with strychnine, neither is α -methoxyphenylacetic acid when heated with brucine, whereas with strychnine it has $[\alpha]_D + 0.32^\circ$. J. J. S.

Di-*p*-methylbenzilic Acid (*pp'*-Tolilic Acid). ERWIN GISIGER (*Ber.*, 1906, 39, 3589. Compare Gattermann, this vol., i, 589).—Di-*p*-methylbenzilic acid is prepared by boiling di-*p*-methylbenzoin with 20 per cent. potassium hydroxide solution through which a current of air is passed; it melts at 135° and gives a blood-red coloration with concentrated sulphuric acid. The *barium* salt, $(C_{16}H_{15}O_3)_2Ba$, forms white leaflets; the *methyl* ester, $C_{17}H_{18}O_3$, crystallises from alcohol in needles and melts at 82°; the *acetyl* derivative, $C_{18}H_{18}O_4$, separates from light petroleum in small crystals, melts at 92°, and is readily hydrolysed. G. Y.

Influence of the Position of the Ethylene Linking on the Electro-affinity and Characters of Unsaturated Alicyclic Acids. GINO ABATI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 220—226).—From a study of the affinity constants of the naphthoic and the hydronaphthoic acids, benzoic acid, phthalic and the hydrophthalic acids, it is seen that, apart from the strongly negative character of the aromatic nucleus, the presence and position of the double linking have no small influence on the energy of an acid. In the $\alpha\alpha$ - and $\beta\gamma$ -positions, the double linking produces a great increase in the value of the electrical conductivity, whilst when it is in the $\alpha\beta$ - or $\gamma\delta$ -position, the values of the conductivity are not much greater than those of the corresponding saturated acids.

The explanation given by Fichter and Pfister (*Abstr.*, 1904, i, 965) of their results on the basis of Thiele's theory of partial valencies is fallacious. According to Thiele's theory, the $\gamma\delta$ -, &c., acids should be as unsaturated as the $\beta\gamma$ -acids, whilst the fact is that they are far weaker than these and have constants not differing greatly from those of the $\alpha\beta$ -acids. This contradiction of Thiele's theory is confirmed by the constants for acids having a double linking in the $\alpha\alpha$ -position with

respect to the two carboxyl groups. For instance, in the case of the four tetrahydrophthalic acids, the Δ^1 -acid should, according to Thiele's theory, be the most saturated and should hence be the least energetic. Instead, however, the constant of this acid is the greatest of the four and is five times that of the Δ^4 -acid, which has six partial valencies. Similar disagreement with this theory is offered by the constants for citraconic, mesaconic, and itaconic acids.

When treated with alkali hydroxides, unsaturated $\beta\gamma$ -acids do not pass completely into the $\alpha\beta$ -isomerides, the reaction being reversible. Further, in the reduction of phthalic acid by means of sodium amalgam, there is a marked tendency to the formation of acids with a double linking in the $\beta\gamma$ -position, although the temperature is kept at about 150° for some three hours and the proportion of sodium hydroxide present in the liquid ultimately reaches 15 or 20 per cent. It is therefore unsafe to assign the $\beta\gamma$ -constitution to acids on the sole ground that they undergo transformation with alkali hydroxides, as has been done by Perkin and Pickles in the case of the tetrahydroisophthalic acids (Trans., 1905, 87, 293). T. H. P.

Hydrophthalic Acids: Affinity Constants of Two New Anhydrides. II. GINO ABATI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 207—210. Compare Abstr., 1905, i, 599).—Conductivity measurements of solutions of the two new hydrophthalic anhydrides (*loc. cit.*) lead to the following values: (1) For $\Delta^{1:3}$ -dihydrophthalic anhydride, $\mu_\infty = 377$ and $K = 0.0798$. (2) For *cis*- Δ^3 -tetrahydrophthalic anhydride, $\mu_\infty = 376$ and $K = 0.0581$.

Titration of aqueous solutions of the anhydrides with barium hydroxide solution, using methyl-orange as indicator, shows that, although they cannot be obtained in the solid state in the form of acids, they behave as acids when dissolved in water; this fact is also shown by the high value of the affinity constants, which are in accord with the constitutions given previously (*loc. cit.*), as it has been repeatedly observed that a double bond in the $\beta\gamma$ -position effects a marked increase in the energy of unsaturated acids. T. H. P.

Hydrophthalic Acids: Transformation by Heat of the New Dihydrophthalic Anhydrides. Characters of the *p*-Methoxyphenylhydrophthalimides. III. GINO ABATI and ANDREA CONTALDI (*Rend. Accad. Sci. Fis. Mat., Napoli*, 1906, [iii], 12, 211—219. Compare preceding abstract).—When heated at about 225° for some two hours, $\Delta^{1:3}$ -dihydrophthalic anhydride (compare Abati and de Bernardinis, Abstr., 1905, i, 599) is converted into another anhydride, which is possibly the $\Delta^{2:5}$ -compound regarded by von Baeyer (Abstr., 1892, 1211) as incapable of existence. When its alcoholic solution is treated with *p*-anisidine, it yields *p*-methoxyphenyl-dihydrophthalimide, which forms white needles melting at 98° , and as it does not correspond with any of the derivatives obtained from the known dihydrophthalic anhydrides, must be regarded as the $\Delta^{2:5}$ -compound. Hence, when the $\Delta^{1:3}$ -anhydride is heated, the double linking in the $\alpha\alpha$ -position migrates to the neighbouring $\alpha\beta$ -position, whilst the other double linking retains its place in the $\beta\gamma$ -position.

p-Methoxyphenyl- $\Delta^{1:3}$ -dihydrophthalimide forms yellow crystals melting at 104° .

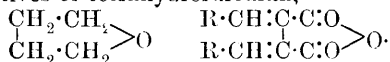
A table is given showing the melting points of the dihydrophthalic and tetrahydrophthalic anhydrides, and the melting points and colours of the *p*-methoxyphenylimides formed from these anhydrides. In general, the anhydrides exhibiting similar physical and chemical characters yield imides similar to one another.

Halochromism is exhibited by all the dihydrophthalimides when dissolved in sulphuric acid, whilst of the tetrahydrophthalimides only the Δ^1 - and Δ^3 -compounds show this phenomenon, a fact which illustrates the influence of the position of the ethylene linking with respect to the phenyldiketopyrrolidine grouping. T. H. P.

β -Benzylideneglutaric Acid. HERMANN A. MÜLLER (*Ber.*, 1906, **39**, 3590—3591. Compare Fittig and Roedel, *Abstr.*, 1895, i, 141; Fittig, *Abstr.*, 1898, i, 11; Fichter and Bauer, *Abstr.*, *ibid.*, 662; Thiele and Meisenheimer, *Abstr.*, 1899, i, 603).—The condensation of benzaldehyde with ethyl tricarballoylate in ethereal solution in presence of sodium ethoxide leads to the formation of β -benzylideneglutaric anhydride, $\text{CHPh}:\text{C} \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix} \text{O}$, which crystallises in colourless, strongly refracting leaflets or long, flat prisms, melts at $44\text{--}45^\circ$, is volatile in a current of steam, and with alkali hydroxides forms salts of β -benzylideneglutaric acid; the acid is unstable and yields the anhydride immediately on liberation. β -Benzylideneglutaranil, $\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}$, formed by heating the anhydride with aniline, crystallises in glistening leaflets and melts at 90° . When boiled with aqueous sodium hydroxide, β -benzylideneglutaric acid yields two acids, melting at 184° and 145° respectively. G. Y.

Colour of Fulgides and of other Unsaturated Compounds. HANS STOBEE (*Annalen*, 1906, **349**, 333—371).—The author cites numerous examples to show that the colour of the fulgenic acids and of similarly constituted substances is to be explained not only by the number and the position of the chromophoric phenyl and carboxyl groups in the carbon chain, but also by the influence of the conjugated double linkings. The fact that $\alpha:\delta$ -diphenyl- $\Delta^{\alpha\gamma}$ -butadiene- δ -carboxylic acid and $\alpha:\delta$ -diphenylfulgenic acid are colourless, whereas $\alpha:\delta$ -diphenyl- $\Delta^{\alpha\gamma}$ -butadiene- γ -carboxylic acid is yellow, is accounted for on stereochemical grounds.

The more pronounced colour of the fulgides is not due to heterocyclic ring formation; examples are quoted to show that such formation results in a diminution or disappearance of the colour. The selective absorption of the fulgides can be brought into harmony with the "quinone" theory, inasmuch as these compounds are ortho- and para-quinonoid derivatives of tetrahydrofurfuran,



In chemical and physical properties they resemble Thiele's fulvenes (*Abstr.*, 1900, i, 298) and "quinonoid" hydrocarbons (*Abstr.*, 1904, i, 491).

The absorption spectra of certain fulgides have been measured in *N*/32 chloroform solution.

Tetramethylfulgide absorbs only in the ultra-violet; the presence of each phenyl group increases by 58μ , the length of the absorption band in the visible spectrum. C. S.

Condensation Products of Gallic Acid with Formaldehyde and Carbamide, or with Formaldehyde and Urethanes. ARNOLD VOSWINKEL (D.R.-P. 171788).—Carbamide (1 mol.) condenses with gallic acid (2 mols.) and formaldehyde, giving rise to a methylene-carbamido-gallic acid having the composition $C_{17}H_{16}O_{11}N_2$. The condensation occurs in dilute alcohol in the presence of mineral acids, and the product is a pale grey powder which melts and decomposes at 210° and has an intensely bitter taste. The compound forms an insoluble basic bismuth salt. G. T. M.

Cetraric Acid. OSCAR SIMON (*Arch. Pharm.*, 1906, **244**, 459—466. Compare Abstr., 1903, i, 98).—The products obtained by treating cetraric acid with aqueous sodium hydroxide and zinc powder have been examined further. From the crude mixture of phenols, 3:5-dihydroxy-1:2-dimethylbenzene, $C_8H_{10}O_2$ (Abstr., 1904, i, 406), has been isolated. When treated with bromine (4 mols.) in chloroform solution, it yields crystalline *dibromo-* and *tribromo-*derivatives; these melt at 98 and 112° respectively, and are converted into the ketobromide, $C_8H_6O_2Br_4$, when treated with excess of bromine in acetic acid solution.

From the same source yellow crystals were obtained which melt at 119 — 121° , contain C 63.4, H 5.5, and have molecular weight 164 (determined cryoscopically in naphthalene); this *substance* does not contain methoxyl; it is soluble in alkali hydroxides and carbonates and gives a green coloration with ferric chloride; when it is treated in the cold with aniline in alcoholic solution, it yields an orange-yellow *anilide*, which melts and decomposes at 189 — 190° , and contains C 73.4, H 6.1, N 7.0; and with excess of bromine in acetic acid solution it forms a *bromide* which melts at 116 — 121° , contains C 17.5, H 1.8, Br 76.6, and is insoluble in aqueous sodium carbonate.

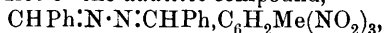
From the resinous mass obtained when the product of the action of aqueous sodium hydroxide and zinc powder is poured into dilute sulphuric acid, a yellow, crystalline *substance* has been obtained which melts at 129 — 132° , contains C 65.5, H 6.1 ($C_{10}H_{12}O_3$?), and has molecular weight 180 (determined cryoscopically in naphthalene); this substance, when treated in alcoholic solution with aniline, forms a red *anilide*, $C_{16}H_{17}O_2N$, which melts and decomposes at 184° , and when treated with a large excess of bromine in acetic acid solution, it yields the ketobromide, $C_8H_6O_2Br_4$.

When cetraric acid, $C_{20}H_{18}O_9$, is treated with bromine, either directly or in acetic acid or chloroform solution, it yields a *bromo-*derivative, probably a mixture of $C_{20}H_{16}O_9Br_2$ and $C_{19}H_{16}O_7Br_2$, which melts at 181 — 185° , still contains methoxyl, and dissolves slowly in aqueous sodium carbonate. C. F. B.

Behaviour of Benzaldehyde in Presence of Iodoxybenzene and under the Action of Light. LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 375—379).—The interaction of benzaldehyde and iodoxybenzene under the influence of light yields: (1) Benzoic acid, by the reaction, $2\text{Ph}\cdot\text{CHO} + \text{PhIO}_2 = 2\text{Ph}\cdot\text{CO}_2\text{H} + \text{PhI}$. (2) A *trimeric benzaldehyde*, $(\text{C}_7\text{H}_6\text{O})_3$, which separates from acetic acid in stable, white crystals melting at 250° . (3) Stilbene, which may be formed either by the reduction of benzaldehyde by iodosobenzene formed as an intermediate product in the oxidation of benzaldehyde to benzoic acid by the iodoxybenzene: $2\text{Ph}\cdot\text{CHO} + 2\text{Ph}\cdot\text{OI} = \text{CHPh}\cdot\text{CHPh} + 2\text{Ph}\cdot\text{IO}_2$; or by the decomposition of a complex oily product, $\text{CHPh}\cdot\text{I}\cdot\text{Ph}$ or $\text{Ph}\cdot\text{I}(\text{CHPh})_2$, which could not be obtained pure, and yields stilbene and iodobenzene on distillation. T. H. P.

Additive Products Formed by Trinitrobenzene with Aromatic Substances containing the Side-chain $\cdot\text{CH}\cdot\text{N}\cdot$. ROBERTO CRUSA (*Gazzetta*, 1906, 36, ii, 94—98).—Benzaldehydephenylhydrazine combines with trinitrobenzene in warm alcoholic solution to form the *additive* compound $\text{CHPh}\cdot\text{N}_2\text{HPh}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_3$, which forms dark red crystals and melts at 134° ; the analogous *trinitrotoluene* derivative, $\text{CHPh}\cdot\text{N}_2\text{HPh}\cdot\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_3$, forms dark red needles and melts at 84° . *Benzaldehydephenylhydrazine picrate*, $\text{CHPh}\cdot\text{N}_2\text{HPh}\cdot\text{C}_7\text{H}_3\text{O}_7\text{N}_3$, prepared similarly by using picric acid, forms blackish-violet needles with a metallic reflex, and melts at 117° . *m-Nitrobenzaldehydephenylhydrazine picrate*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}_2\text{HPh}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, crystallises in chestnut coloured needles with a violet sheen and melts at 118° .

Benzylideneazaine combines with trinitrotoluene in alcoholic solution, giving yellow needles of the *additive* compound,



which melts at 97 — 98° . *Benzylideneazaine picrate*, $\text{C}_{14}\text{H}_{12}\text{N}_2\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, forms small, canary-yellow needles and melts at 148° . *Furfuralazine picrate*, $(\text{C}_4\text{H}_3\text{O}\cdot\text{CH})_2\text{N}_2\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, crystallises from alcohol in greenish-yellow needles, darkens at 155° , and melts and decomposes at 157° . *Benzylideneaniline picrate*, $\text{CHPh}\cdot\text{NPh}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, crystallises in golden-yellow needles and melts at 183° . *Salicylideneaniline picrate*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NPh}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, forms lustrous, yellow needles and melts at 153 — 154° . *Cinnamylideneaniline*, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{NPh}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, crystallises in orange-yellow needles or plates and melts at 139° .

W. A. D.

Some Aromatic Aldehydes and Ketones. KARL AUWERS (*Ber.*, 1906, 39, 3757—3764. Compare Auwers and Hessenland, *Abstr.*, 1905, i, 434).—*p*-Methylhydrocinnamaldehyde (von Miller and Rohde, *Abstr.*, 1890, 978) is a colourless oil which boils at 220 — 230° under atmospheric pressure, has a sp. gr. 0.9928 at $18.5^\circ/18.5^\circ$, and forms a *semicarbazone*, $\text{C}_{11}\text{H}_{15}\text{ON}_3$, crystallising in long, flat, glistening needles and melting at 170 — 171° . *p*-Ethylbenzoylmethyl chloride, $\text{C}_6\text{H}_4\text{Et}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$, prepared by Friedel and Craft's synthesis from ethylbenzene and chloroacetyl chloride, crystallises from light petroleum in white scales, melts at 38 — 39° , boils at 145 — 148° under 8 mm. pressure, and forms a *semicarbazone*, $\text{C}_{11}\text{H}_{14}\text{ON}_3\text{Cl}$, crystallising in

slender, white needles and melting at 153—154°. *p*-Ethylbenzoyl-methyl acetate, $C_6H_4Et \cdot CO \cdot CH_3 \cdot OAc$, prepared by boiling the chloride with potassium acetate and glacial acetic acid, crystallises in white prisms, melts at 61—62°, and when boiled with alcoholic sodium hydroxide yields the *carbinol*, $C_6H_4Et \cdot CO \cdot CH_2 \cdot OH$. This crystallises in yellow leaflets, melts at 67—68°, and has a sweet flavour; the *semicarbazone*, $C_{11}H_{15}O_2N_3$, crystallises in white scales and melts at 161°. *p*-Ethylphenylacetaldehyde, $C_6H_4Et \cdot CH_2 \cdot CHO$, prepared by reducing the ketonic alcohol with sodium amalgam in aqueous alcoholic carbonate solution through which a current of carbon dioxide is passed, and treatment of the resulting glycol with concentrated sulphuric acid, is obtained as an oil; this has an odour of cuminaldehyde, and forms a *semicarbazone*, $C_{11}H_{15}ON_3$, crystallising in slender, white needles and melting at 162—164°.

p-Methylbenzoylmethyl chloride melts at 57—58° (compare Kuncell, Abstr., 1897, i, 282; Collet, Abstr., 1898, i, 139; Ryan, *ibid.*, 649); the acetate melts at 85—86° (83—83.5°, Collet, 1898, i, 123). *p*-Methylbenzoylcarbinol, $C_6H_4Me \cdot CO \cdot CH_2 \cdot OH$, crystallises in light yellow prisms, melts at 89—89.5°, and forms a *semicarbazone*, $C_{10}H_{13}O_2N_3$, crystallising in white needles and melting at 165°. Reduction of the ketonic alcohol with sodium amalgam and treatment of the product with concentrated sulphuric acid leads to the formation of only a small amount of an oil, which has a characteristic odour of elderberries, and forms a *semicarbazone*, $C_{10}H_{13}ON_3$, melting at 208°. A small amount of the same *semicarbazone*, but melting at 212—213°, is obtained from the product formed on boiling *p*-methyl- $\beta\beta$ -dichloroethyl benzene with aqueous potassium hydroxide.

o-Chloro-*p*-methylhydratropic acid, $C_6H_4Me \cdot CClMe \cdot CO_2H$, prepared by the action of hydrogen cyanide on *p*-methylacetophenone (compare Janssen, Abstr., 1889, 596) and treatment of the product with concentrated hydrochloric acid at 130° (Spiegel, Abstr., 1881, 277), crystallises from carbon disulphide and melts at 116—118°.

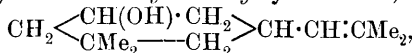
p-Methylhydratropaldehyde, $C_6H_4Me \cdot CHMe \cdot COH$, prepared by the action of ethyl chloroacetate and sodamide on *p*-methylacetophenone (compare Claisen, Abstr., 1905, i, 287), boils at 227—228° under atmospheric pressure, and is identical with the aldehyde obtained from cymene by Etard's reaction; it forms a *semicarbazone* crystallising in slender, white needles melting at 155—157°.

The supposed aldehyde-*semicarbazone* previously obtained (Abstr., 1905, i, 434) from dichloro-*p*-cymic acid is now found to be the *semicarbazone* of *p*-tolylacetone; it is accompanied by a small amount of a *semicarbazone* of an aldehyde which remains in the mother liquors on recrystallisation.

5-Ethylsalicylaldehyde, $OH \cdot C_6H_3Et \cdot COH$, prepared from *p*-ethylphenol by Reimer's synthesis, is an oil; the *semicarbazone*, $C_{10}H_{13}O_2N_3$, crystallises in nacreous leaflets and melts at 208°. G. Y.

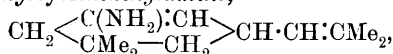
Synthesis of a Ketone Isomeric with Xylitane. EMIL KNOEVENAGEL and RUDOLF SCHWARTZ (*Ber.*, 1906, 39, 3441—3451. Compare Kerp and Müller, Abstr., 1898, i, 265; Pinner, Abstr., 1882, 941).—A compound isomeric with Pinner's xylitane may be

synthesised by the action of sodium ethoxide on a mixture of ethyl acetoacetate and acetophenone; it is represented as *isobutenyldimethylcyclohexenone*, $\text{CH}_2 \begin{smallmatrix} \text{CO} \text{---} \text{CH} \\ \text{CMe}_2 \text{---} \text{CH}_2 \end{smallmatrix} \text{C} \cdot \text{CH} \cdot \text{CMe}_2$, and distils at $132\text{--}134^\circ$ under 12 mm. pressure, or at 246° under atmospheric pressure. It is not readily volatile with steam, and has a sp. gr. 0.9365 at $19^\circ/4^\circ$. The molecular refraction is higher even than what would be required for the enolic compound. It yields a *tetrabromide*, which is extremely unstable, a *phenylhydrazone* melting at $80\text{--}81^\circ$, an *oxime*, $\text{C}_{12}\text{H}_{19}\text{ON}$, melting at various temperatures between 85° and 108° , and a *semicarbazone* melting at $167\text{--}168^\circ$. When reduced with sodium and alcohol, it yields *isobutenyldimethylcyclohexanol*,



which boils at $122\text{--}123^\circ$ under 12 mm. pressure, and has a sp. gr. 0.8886 at $23.5^\circ/4^\circ$ and n_D 1.4675 at 23.5° . The *dibromide* is unstable, and the *acetate* distils at $244\text{--}247^\circ$. When oxidised with chromic acid mixture, the alcohol yields the corresponding ketone *isobutenyldimethylcyclohexanone*, $\text{C}_{12}\text{H}_{20}\text{O}$, which boils at $109\text{--}110^\circ$ under 12 mm. pressure. It has a sp. gr. 0.8823 at $19.5^\circ/4^\circ$ and n_D 1.1397 at 19.5° . With phosphoric oxide, the alcohol yields *isobutenyldimethylcyclohexene*, $\text{CH}_2 \begin{smallmatrix} \text{CH}=\text{CH} \\ \text{CMe}_2 \text{---} \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CH} \cdot \text{CMe}_2$, boiling at $195\text{--}196^\circ$. It has a sp. gr. 0.8246 at $23^\circ/4^\circ$ and n_D 1.4653 .

isoButenyldimethylcyclohexenylamine,



obtained by reducing the oxime, boils at $108\text{--}112^\circ$ under 14 mm. pressure. A by-product is an oil boiling at $150\text{--}160^\circ$ under 10 mm. pressure. The base is unstable, decomposing slowly with formation of ammonia. The *sulphate*, $\text{C}_{12}\text{H}_{21}\text{N} \cdot \text{H}_2\text{SO}_4$, melts at $115\text{--}116^\circ$, and the *phenylthiocarbamide* at $129\text{--}130^\circ$. J. J. S.

Condensation Products of High Molecular Weight from Acetone. Alkaline Condensation of Acetone. EMIL KNOEVENAGEL and LEO BLACH (*Ber.*, 1906, 39, 3451—3457).—*iso*Butenyldimethylcyclohexenone (compare preceding abstract) yields acetone and *iso*-acetophorone when boiled with concentrated formic acid. Two products, isomeric with *isobutenyldimethylcyclohexenone*, have been prepared from the higher fractions obtained by the action of sodium ethoxide on acetone. The first, α -*isoxylitone* is identical with Kerp and Müller's xylitone. It boils at $117\text{--}119^\circ$ under 11 mm. pressure, has a sp. gr. 0.9396 at $16^\circ/4^\circ$ and n_D 1.5249 at 16° ; it yields an oily oxime, and a semicarbazone which melts at about 159° . The second compound, β -*isoxylitone*, distils at $129\text{--}131.5^\circ$ under 11 mm. pressure, has a sp. gr. 0.9513 at $18^\circ/4^\circ$, n_D 1.5182 at 18° , and yields a *semicarbazone* melting at 175° . J. J. S.

Condensation Products of High Molecular Weight from Acetone. Acid Condensation of Acetone. EMIL KNOEVENAGEL and HANS BEER (*Ber.*, 1906, 39, 3457—3466. Compare preceding abstracts).—The following fractions have been isolated from the

products of high boiling point obtained by the condensation of acetone with hydrochloric acid: 120—122°, 127—129°, 137—139°, and 141—144°, all under a pressure of 11 mm. The first fraction has the composition $C_{15}H_{24}O_2$ and yields a semicarbazone which melts at 148°. The fraction 127—129° appears to be identical with Pinner's xylitone (Abstr., 1882, 941). With semicarbazide it yields a derivative melting at 151°, and oily products with hydroxylamine or phenylhydrazine. It is not identical with synthetical xylitone or with α - and β -isoxylitones. The analytical data of fractions three and four agree with the formula $C_{19}H_{26}O$.

From a second specimen of Kahlbaum's high boiling products, two fractions, 128—130° and 140—142°, were obtained. The first fraction, after removal of small amounts of oxygenated compound by means of sodium hydrogen sulphite, gave analytical data agreeing with the formula $C_{15}H_{24}$. It has a sp. gr. 0.9062 at 16°/4° and n_D 1.5338, and may probably be a sesquiterpene. The second fraction gives analytical results agreeing with either $C_{18}H_{30}$ or $C_{21}H_{36}$. J. J. S.

Nitro- and Amino-propiofenones. EZIO COMANDUCCI and LUIGI PESCI TELLI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 286—291).—By the action of fuming nitric acid on propiofenone under various conditions, the authors have obtained the three nitro-propiofenones.

o-Nitropropiofenone (?), $NO_2 \cdot C_6H_4 \cdot COEt$, crystallises from alcohol in yellow needles melting at 85°, and is soluble in water, ether, chloroform, or benzene.

m-Nitropropiofenone (?) (compare Barry, Abstr., 1874, 74) crystallises from alcohol in pale, yellow needles melting at 98°, dissolves in water, benzene, ether, chloroform, or light petroleum, and yields a white, crystalline product with sodium hydrogen sulphite.

p-Nitropropiofenone (?) separates from ether in yellowish-white crystals melting at 114°, dissolves rapidly in alcohol, chloroform, benzene, or alkali solution and to a less extent in water or light petroleum, and forms a white, crystalline compound with sodium hydrogen sulphite.

The aminopropiofenones obtained by reducing the *o*- and *p*-nitro-compounds are white, and dissolve in water, alcohol, or ether, whilst that from the *m*-derivative is a syrup with an odour of strawberries and is soluble in water or alcohol; all of them give the alkaloid reactions. The *hydrochloride* of the *m*-amino-derivative decomposes at 170° and melts at a slightly higher temperature, whilst those of the ortho- and para-compounds decompose without melting at about 200°. (Compare Kunckell, Abstr., 1900, i, 664.) T. H. P.

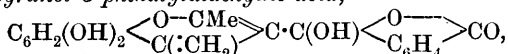
Migration of the Phenyl Group; Mode of Fixation of Hypiodous Acid and the Elimination of Hydrogen Iodide. MARC TIFFENEAU (*Compt. rend.*, 1906, 143, 649—651. Compare Abstr., 1902, i, 666; 1904, i, 63; this vol., i, 662, 724).—Hydrocarbons of the general formula $R\text{ArC}:\text{CHR}'$ (where R and R' represent alkyl groups which may be identical or different or replaced by

hydrogen, and Ar represents an aryl group) form iodohydrins, which, on treatment with silver nitrate, are converted into the ketones, $R \cdot CO \cdot CHArR'$. Thus, α -phenyl- Δ^a -isoamylene, $CHPh:CHPr^B$, boiling at $204-206^\circ$, yields α -phenylisovaleraldehyde, $CHPhPr^B:CHO$, boiling at $222-223^\circ$. β -Phenyl- Δ^a -amylene, $CH_2:CPhPr^a$, boiling at $198-200^\circ$, and having a sp. gr. 0.9138 at 0° , yields benzyl propyl ketone, $CH_2Ph \cdot COPr^a$ (Blaise, Abstr., 1902, i, 164), which boils at $237-239^\circ$, has a sp. gr. 0.9889 at 0° , and forms a semicarbazone melting at 189° . β -Phenyl- Δ^B -butylene, $CPhMe:CHMe$, yields benzyl methyl ketone which has a sp. gr. 0.997 at 0° (Darzens, this vol., i, 63). β -Phenyl- Δ^B -amylene, $CPhMe:CHEt$, boiling at $199-201^\circ$, yields α -phenyl-propyl methyl ketone, $CHPhEt:COMe$, which boils at $225-227^\circ$, has a sp. gr. 0.979 at 0° , and forms a semicarbazone melting at 188° .

The iodohydrin of α -phenyl- Δ^a -isobutylene, $CHPh:CMe_2$, when treated with silver nitrate, yields a mixture of phenylisobutaldehyde (Abstr., 1902, i, 666), and phenylbutylene oxide, $O \begin{smallmatrix} \text{CHPh} \\ \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \\ \text{CMe}_2 \end{smallmatrix}$, which boils at $213-215^\circ$; it is probable that in the case of this hydrocarbon the two iodohydrins, $CHPhI \cdot CM_2 \cdot OH$ and $OH \cdot CH \cdot Ph \cdot CIME_2$, are formed, which, on elimination of hydrogen iodide, yield the corresponding ethylene oxide and unstable vinyl alcohol respectively, the latter changing into the isomeric aldehyde. M. A. W.

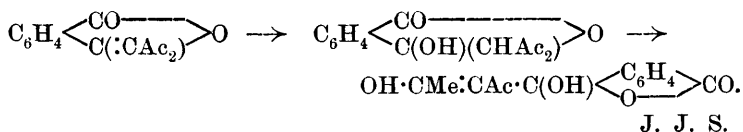
[*p*-Dimethylaminobenzylideneacetone.] Correction. FRANZ SACHS and WILLY LEWIN (*Ber.*, 1906, 39, 3785).—*p*-Dimethylaminobenzylideneacetone sinters at 130° and melts at $134-135^\circ$ and not at 230° and $234-235^\circ$ as given previously (Abstr., 1903, i, 37. Compare Rupe and Siebel, this vol., i, 859). G. Y.

Combination of Phthalylacetylacetone with Pyrogallol. CARL BÜLOW and MAX DESENISS (*Ber.*, 1906, 39, 3664—3667. Compare Abstr., 1901, i, 475; 1902, i, 554; 1905, i, 149, 294, 529; this vol., i, 588).—The lactone of 7:8-dihydroxy-2-methyl-4-methylene-1:4-benzopyranol-3-phthalylaldehydic acid,



is obtained in the form of its hydrochloride by passing hydrogen chloride into an acetic acid solution of pyrogallol and phthalylacetylacetone and keeping the mixture at 0° . The hydrochloride, $C_{19}H_{14}O_6 \cdot HCl \cdot 1.5H_2O$, crystallises from alcohol containing hydrogen chloride in red prisms, which decompose at about 109° . It dissolves in acetone, alcohol, benzene, or glacial acetic acid, but is insoluble in ether, and is readily hydrolysed by water. The picrate, $C_{25}H_{17}O_{13}N_3$, forms red crystals decomposing at $195-200^\circ$, and soluble in water and most organic solvents.

It is suggested that in the above condensation the phthalylacetylacetone forms an additive compound with water, and this then passes into the enolic form,



Sodium Hyposulphite as a Reducing Agent. II. EUGÈNE GRANDMOUGIN (*Ber.*, 1906, **39**, 3561—3564. Compare this vol., i, 716).—In many reductions the use of sodium hyposulphite is to be preferred to that of the usual reducing agents, as in the preparation of β -naphthaquinone from Orange II. (Grandmougin and Michel, *Abstr.*, 1892, 861), or of 1:4-diaminonaphthalene from 4-benzeneazo-1-naphthylamine (Bamberger and Schieffelin, *Abstr.*, 1889, 495).

Sodium hyposulphite may be used in the reduction of compounds other than those containing an azo-group. Nitrobenzene gives poor yields of aniline; *o*-nitrophenol is reduced to *o*-aminophenol; in these cases sodium sulphide is a better reducing agent than the hyposulphite. The quinones: benzoquinone, β -naphthaquinone, and phenanthraquinone, are readily reduced by sodium hyposulphite to the corresponding quinols; oxanthranol is obtained more readily by reduction of anthraquinone in this manner than by Graebe and Liebermann's method (this Journal, 1872, **25**, 139).

Benzil is reduced by sodium hyposulphite to benzoin.

G. Y.

Oxidation of Diaminophenols. FRIEDRICH KEHRMANN and H. PRAGER (*Ber.*, 1906, **39**, 3437—3441).—When a solution containing 2:4-diaminophenol hydrochloride and ferric chloride is mixed with sodium dichromate solution, greenish-black, glistening crystals of *aminobenzoquinoneimide dichromate*, $2\text{NH} \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{O} \cdot \text{H}_2\text{Cr}_2\text{O}_7$, are deposited. They dissolve to a certain extent in cold water, yielding a red solution and are completely decomposed by hot water. The *picrate*, $\text{C}_{12}\text{H}_9\text{O}_8\text{N}_5$, forms chocolate-brown crystals.

Corresponding salts of benzoquinoneimides have been obtained from 2:4-diamino-*o*-cresol; the *nitrate*, $\text{NH} \cdot \text{C}_6\text{H}_2\text{Me}(\text{NH}_2) \cdot \text{O} \cdot \text{HNO}_3$, is readily obtained on the addition of solid sodium nitrate to a mixture of diaminocresol hydrochloride and ferric chloride. It dissolves in water or alcohol, yielding solutions with a bluish-red colour. The *dichromate* and *picrate* have also been prepared.

The *nitrate* of amino-*m*-methylbenzoquinoneimide forms blackish-red needles readily soluble in water; the *dichromate* is readily soluble; the *mercurichloride* is sparingly soluble, and crystallises in blackish-red needles.

Corresponding reddish-violet salts have been obtained from diamino-thymol.

J. J. S.

1:4-Anthraquinone. C. HASLINGER (*Ber.*, 1906, **39**, 3537—3538. Compare Dienel, this vol., i, 290).—The melting point of 1:4-anthraquinone formerly given as 206° must be regarded as a decomposition point, owing to the darkening of the substance which occurs even at 190° . The successive stages of the process of converting 1:4-anthraquinone into quinizarin take place very readily, the diacetylquinizarin

being hydrolysed by cold concentrated acid instead of alcoholic potash as formerly described. G. T. M.

Preparation of Alkylated Aryl-*p*-diaminoanthraquinone-sulphonic Acid. FARBERWERKE VORM. MEISTER, LUCIUS, and BRÜNING (D.R.-P. 174131).—It has been found that the alkyl sulphates behave both as alkylating and sulphonating agents towards the aryl-diamino-anthraquinones, so that alkylated aryl-*p*-diaminoanthraquinonesulphonic acids are obtained in one operation.

1-Amino-4-*p*-toluidinoanthraquinone is in this way converted into the colouring matter 4-*p*-toluidino-4-dimethylaminoanthraquinonesulphonic acid and 1:5-diamino-4:8-di-*p*-toluidinoanthraquinone furnishes 4:8-di-*p*-toluidino-1:5-tetramethyl-diaminoanthraquinonesulphonic acid which is isolated in the form of its sodium salt. G. T. M.

Derivatives of the Aminoalizarins. GUSTAV SCHULTZ and J. ERBER (*J. pr. Chem.*, 1906, [ii], 74, 275—296. Compare Abstr., 1902, i, 299).—The α -diacetyl-aminoalizarin melting at 205° crystallises from alcohol in glistening, golden-yellow needles, decomposes when sublimed, forming acetic acid and a red sublimate of α -aminoalizarin.

α -Dibenzoylaminoalizarin melts above 310°, and gives a red coloration with concentrated sulphuric acid.

β -Dibenzoylaminoalizarin gives a dark violet coloration with, but does not dissolve in, aqueous sodium hydroxide, becoming yellow again on addition of hydrochloric acid, and is then soluble in cold sodium hydroxide, forming a bluish-violet solution. With concentrated sulphuric acid it gives a red coloration, and after five minutes on addition of water yields benzoyl- β -aminoalizarin, $C_{21}H_{13}O_5N$, which crystallises from nitrobenzene in small, matted, dark green needles, melts at 275°, sublimes with partial decomposition forming yellow needles, is not hydrolysed by boiling concentrated hydrochloric acid, and gives with concentrated sulphuric acid a red, with aqueous sodium hydroxide a blue, coloration.

Prolonged action of concentrated sulphuric acid on the β -dibenzoylamino-derivative leads to the formation of a *product* which crystallises from nitrobenzene in yellowish-brown needles, melts at 320°, and closely resembles the monobenzoyl derivative.

α -Diazoalizarin sulphate (compare Brasch, Abstr., 1891, 1077) is formed by the action of sodium nitrite on α -aminoalizarin in ice-cooled, concentrated sulphuric acid solution; it separates on moderate dilution with alcohol in glistening, yellowish-brown needles, decomposes at about 140°, dissolves in much alcohol forming a brownish-violet solution becoming orange-yellow when heated, and when treated with aqueous alkali hydroxides at the ordinary temperature forms a reddish-violet solution which evolves nitrogen and becomes blue, the diazo-sulphate being converted into alizarin. When sublimed or boiled with dilute acids it yielded purpurin (Farbwerke vorm. Meister, Lucius, and Brüning, D.R.-P. 97688). The α -diazo-hydroxide is obtained as a brown, insoluble residue on treatment of the diazo-sulphate with water.

Diazotisation of β -aminoalizarin leads to the formation of the β -diazio-sulphate, which separates to a small extent in yellow crystals. On addition of water or alcohol to the acid solution, the β -diazio-hydroxide, $C_{14}H_5O_2(OH)_2 \cdot N_2 \cdot OH$, is thrown down as a scarlet or orange-red precipitate; this darkens on exposure to air, decomposes at 135° , and detonates when heated. It is decomposed by boiling dilute acids, aqueous alkali hydroxides, or alcohol, forming alizarin, only after prolonged drying or contact with dilute sulphuric acid.

With potassium iodide the diazo-derivatives of alizarin form iodo-alizarins which dye mordanted stuffs brown. Azo-dyes cannot be obtained by coupling α -diazio-alizarin sulphate in alkaline or acid solution, whilst only a small amount of an unstable dye is formed by coupling β -diazioalizarin hydroxide with R-salt in alkaline solution.

Experiments are quoted to show that the stability of the diazo-derivatives of benzene and naphthalene increases with the size of the nucleus; it was to be expected, as is found, that the diazo-derivatives of anthracene would be still more stable. β -Diazioalizarin hydroxide resembles to some extent the diazonaphthalenes; in the α -derivatives the characteristics of the diazo-compounds are still less prominent.

When heated with sulphuric acid containing 20—40 per cent. of the anhydride, and poured into water, α -aminoalizarin yields a reddish-brown precipitate which, when boiled with water, is converted into α -aminoalizarin-3-sulphonic acid (4-amino-1:2-dihydroxyanthraquinone-3-sulphonic acid), $C_{14}H_4O_2(OH)_2(NH_2) \cdot SO_3H$ (D.R.-P. 82938); this crystallises from alcohol in microscopic, nodular aggregates, is almost insoluble in ether, and forms a dark violet, insoluble barium salt, and a silver salt crystallising in microscopic, reddish-brown needles. Oxidation of the sulphonic acid leads to the formation of phthalic acid. When diazotised and heated in concentrated acid solution at 50 — 60° , α -aminoalizarin-3-sulphonic acid yields purpurin-3-sulphonic acid, which is isolated in the form of its sparingly soluble potassium salt, $C_{14}H_7O_8SK$, and is probably identical with the acid obtained by sulphonation of purpurin or by oxidation of alizarinsulphonic acid with nitric acid (D.R.-P. 84774), together with alizarin-3-sulphonic acid, which is considered to be identical with the acid formed by the action of fuming sulphuric acid on alizarin.

Purpurin-3-sulphonic and alizarin-3-sulphonic acids are formed also by boiling diazotised 4-aminoalizarin-3-sulphonic acid with aqueous sodium hydroxide. G. Y.

Preparation of a Base, $C_{10}H_{17}ON$, from Pulegone. FRIEDRICH W. SEMMLER (D.R.-P. 173775).— α -Anhydropulegonehydroxylamine, $C_{10}H_{17}ON$, produced by warming pulegonehydroxylamine with concentrated hydrochloric acid at 100° , when purified by means of its picrate, boils at 91° under 8 mm. pressure. The new base readily takes up four hydrogen atoms, and the resulting tetrahydro-base, $C_{10}H_{21}OK$, gives a characteristic thiocarbamide melting at 132° .

Benzylidene- α -anhydropulegonehydroxylamine, $CHPh:C_{10}H_{15}ON$, obtained by condensing the α -anhydro-base with benzaldehyde in the presence of sodium ethoxide, crystallises from ether in needles melting at 105 — 106° ; its picrate melts at 125 — 126° .

By the action of hydriodic acid on pulegonehydroxylamine, reduction and dehydration occur simultaneously, and a new base is obtained having the composition $C_{10}H_{19}ON$. G. T. M.

Chlorohydrochlorides of Pinene and Firpene. GEORGE B. FRANKFORTER and FRANCIS C. FRARY (*J. Amer. Chem. Soc.*, 1906, 28, 1461—1467).—The pinene used in these experiments was prepared from ordinary turpentine by distilling with steam, drying, and redistilling until it boiled constantly at 156 — 157° ; it had a sp. gr. 0.8647 at 20° , n_D 1.46336 at 20° , and $[\alpha]_D +14.34^{\circ}$. The firpene was obtained from the western fir by distilling the crude pitch with steam and redistilling the terpene several times; the product had the composition $C_{10}H_{16}$, and differed from pinene in both chemical and physical properties. It boiled at 153 — 153.5° and had a sp. gr. 0.8598 at 20° , n_D 1.47299 at 20° , and $[\alpha]_D -47.2^{\circ}$. A method is described for the preparation of the hydrochlorides of these terpenes.

Pentachloropinene hydrochloride, $C_{10}H_{11}Cl_5.HCl$, obtained by treating a chloroform solution of pinene hydrochloride with potassium permanganate and hydrochloric acid, forms deliquescent, isometric crystals and melts at 173 — 174° . An attempt to prepare the compound from pinene itself instead of the hydrochloride was unsuccessful.

Nonachloropinene hydrochloride, $C_{10}H_7Cl_9.HCl$, obtained by the action of chlorine in bright sunlight on a solution in carbon tetrachloride of an uncrystallisable substance formed in the preparation of pentachloropinene hydrochloride, crystallises from alcohol, melts at 263 — 264° (uncorr.) and is very soluble in ether, benzene, chloroform, or carbon tetrachloride.

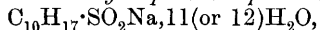
Firpene hydrochloride, $C_{10}H_{16}.HCl$, melts at 130 — 131° , and is more volatile than pinene hydrochloride and more soluble in most of the ordinary solvents.

Dichlorofirpene hydrochloride, $C_{10}H_{14}Cl_2.HCl$, is less volatile and less soluble in alcohol than pinene hydrochloride.

Firpene hydrobromide, $C_{10}H_{16}.HBr$, forms feathery crystals and melts at 102° .

By the action of nitrosyl chloride on firpene an oily, uncrystallisable substance is produced. E. G.

Dihydropinenesulphinic Acid, Dihydropinenecarbithionic Acid, Thioborneol, and Thiocamphor. JOSEF HOUBEN and HANS DOESCHER (*Ber.*, 1906, 39, 3503—3509. Compare Borsche and Lange, this vol., i, 679).—*Sodium dihydropinenesulphinic acid*,



prepared by passing sulphur dioxide into an ethereal solution of the magnesium compound of pinene hydrochloride and subsequently neutralising the portion soluble in ether with sodium carbonate, crystallises from water in well-defined, white leaflets having a faint characteristic odour.

Dihydropinenesulphinic acid, when set free by sulphuric acid from the foregoing salt, separates as a colourless oil slowly solidifying to needles on cooling in ice-water; it melts at 64° and probably is hydrated. When heated under 12 mm. pressure, it decomposes, yield-

ing small quantities of camphane, and a similar change occurs on distilling it in steam.

Dihydropinenecarbithionic acid, obtained by adding carbon disulphide to the ethereal solution of the magnesium compound of pinene hydrochloride, is a brown oil having a camphoraceous odour; it is extremely decomposable, but yields characteristic metallic salts.

The interaction of sulphur and the magnesium compound of pinene hydrochloride leads to the production of thioborneol together with smaller quantities of dihydrodicamphene, bornyl disulphide, and other substances containing a larger proportion of sulphur.

On oxidation with dilute chromic acid at moderate temperatures, thioborneol is converted almost quantitatively into bornyl disulphide; at higher temperatures the latter decomposes into thioborneol and thiocamphor, so that by working under these conditions all the sulphur compounds obtained from the magnesium compound of pinene hydrochloride can be converted into thiocamphor. On exposure to the air or more rapidly by the action of oxygen, thiocamphor evolves sulphur dioxide and becomes converted into a colourless, odourless substance melting at 168° , which is probably bornyl sulphide. G. T. M.

Pitch [Oleo-resin] and Terpenes of the Norway Pine and the Douglas Fir. GEORGE B. FRANKFORTER (*J. Amer. Chem. Soc.*, 1906, 28, 1467—1472).—The wood of the Norway pine (*Pinus resinosa*) yields from 6.2 to 42.6 per cent. of "pitch" [oleo-resin], which is obtained as a colourless, mobile liquid, has a sp. gr. 0.8137, n_D 1.47869, $[\alpha]_D + 4^{\circ}$, and consists of about 22.1 per cent. of oil of turpentine, 77.3 per cent. of colophony, and 0.6 per cent. of water. The terpene obtained from this oleo-resin by steam distillation boils at 153 — 154° , has a sp. gr. 0.8636, n_D 1.47127, and $[\alpha]_D + 17.39^{\circ}$. The terpene obtained by the process of destructive distillation boils at 158 — 160° , has a sp. gr. 0.8666, n_D 1.4716, and $[\alpha]_D - 7.56^{\circ}$.

The wood of the Douglas fir (*Pseudotsuga taxifolia*) contains from 11.6 to 42.4 per cent. of oleo-resin which when first obtained is a clear, colourless liquid, but when left in the air becomes viscous and coloured. This product has a peculiar, aromatic odour, a sp. gr. 0.9821, n 1.51745, and $[\alpha]_D - 8.82^{\circ}$, and contains about 22 per cent. of turpentine. The terpene obtained from this oleo-resin by steam distillation boils at 153.5 — 154° , has a sp. gr. 0.8621, n_D 1.47299, and $[\alpha]_D - 47.2^{\circ}$. The terpene obtained by destructive distillation boils at 157 — 160° , has a sp. gr. 0.8662, n_D 1.47246, and $[\alpha]_D - 29.4^{\circ}$. All the physical constants were determined at 20° . E. G.

Volatile Oil of Juniperus Phoenicea. J. RODÉ (*Bull. Soc. chim.*, 1906, [iii], 35, 922—925. Compare Umney and Bennett, *Pharm. J.*, 75, 827).—The oil is bright yellowish-green and has an odour recalling those of juniper and savin, more especially the former. It is soluble in four to five times its volume of alcohol (90°), has a sp. gr. from 0.867—0.868 and its rotation in a 100 mm. tube varies from $2^{\circ}54'$ to $4^{\circ}10'$. The yield is from 0.45 to 0.5 per cent. of the plant.

The oil contains 92.3 per cent. of terpenes, principally pinene with

traces of phellandrene and camphene and possibly dipentene, and 6.51 per cent. of other constituents boiling above 180°. T. A. H.

Oil of Myrrh. KURT LEWINSOHN (*Arch. Pharm.*, 1906, **244**, 412—435. Compare Tschirch and Bergmann, this vol., i, 197).—Three samples of commercial oil were examined, and one that was freshly prepared in the laboratory by distilling heerabol-myrrh with steam without addition of alkali. Three samples, including the fresh one, contained cuminaldehyde up to 1 per cent.; all samples contained small quantities of eugenol and *m*-cresol, and of acetic and palmitic acids, the latter being present as esters in the fresh sample, in the free state in the commercial samples. When one commercial sample, freed from these constituents, was mixed with light petroleum, a resin separated in amount equal to about 30 per cent. of the oil; this contained oxygen, and, when reduced in amyl-alcoholic solution with sodium, yielded a sesquiterpene apparently identical with cadinene. By fractional distillation of the oils over metallic sodium, pinene, dipentene, and limonene were isolated; it is an open question whether the dipentene is present in the original oils.

From one commercial sample, a fourth *terpene*, $C_{10}H_{16}$, also was isolated, possibly an intermediate stage between limonene and dipentene; it boils at 78—80° under 20 mm. pressure, has a sp. gr. 0.847 at 20°, and $[\alpha]_D + 80^\circ$ at 20°; it forms a *tetrabromide* melting at 115°, a *monohydrochloride* melting at 6°, and an oily *nitrosochloride*. Two other, possibly new, *sesquiterpenes*, $C_{15}H_{24}$, were isolated also from the other two commercial samples; one, forming 24 per cent. of the oil from which it was obtained, boiled at 151—154° under 15 mm. pressure and had a sp. gr. 0.911 at 21°; the other boiled at 163—168° under 12 mm. pressure, and had sp. gr. 0.926 at 20° and $[\alpha]_D + 22.75^\circ$ at 20°. C. F. B.

Preparation of Normal Esters from Santal Oil. KNOLL & Co. (D.R.-P. 173240).—The disadvantages attending the therapeutic application of santal oil and its known derivatives are overcome by converting the oil into an alkyl carbonate or an ester of an aromatic monobasic acid.

The *benzoyl* derivative of santal oil prepared either by heating the oil with benzoic anhydride at 110° or by condensing it with benzoic chloride in the presence of pyridine, has a sp. gr. 1.047 at 15°, and boils at 236—238° under 15 mm. pressure. This preparation is not volatile in steam and may thus be separated from the unbenzoylated santal oil.

The *salicyl* derivative is made by heating santal oil or pure santalol with salol and a small proportion of sodium hydroxide under diminished pressure until the elimination of phenol is complete; the sp. gr. is 1.07, and the salicylsantalol boils with partial decomposition at 250—260° under 20 mm. pressure.

Santalyl ethyl carbonate, prepared by condensing santal oil with ethyl chlorocarbonate in pyridine, boils at 180—185° under 25 mm. pressure, and has a sp. gr. 1.010 at 15°. The interaction of carbonyl chloride and santal oil under these conditions gives rise to the normal santalyl carbonate. G. T. M.

Baptisia Glucosides. K. GORTER (*Arch. Pharm.*, 1906, **244**, 401—405. Compare *Abstr.*, 1898, i, 39).— ψ -Baptisin has now been isolated from the roots of *Baptisia tinctoria*.

ψ -Baptigenin melts at 303—304°. Its sodium derivative has the composition $C_{15}H_{11}O_6Na, H_2O$; when it is heated at 150° with ethyl iodide and a little alcohol, it is converted partially into a new substance which melts at 169°, contains C 71.3, H 4.9 per cent. ($C_{12}H_{10}O_3$?), dissolves readily in hot alcohol, and gives no coloration with ferric chloride in acetone solution. C. F. B.

Attempts to Prepare Aloe-emodin. OTTO A. OESTERLE (*Chem. Centr.*, 1906, ii, 882; from *Schweiz. Woch. Pharm.*, **44**, 509—512).—Aloetic acid was reduced by means of a very large excess of 33 per cent. potassium hydrogen sulphide to hydroaloetic acid; the latter compound when diazotised and heated with alcohol gave a small quantity of aloe-emodin. *Hydroaloetic acid* is a bluish-black, amorphous powder, which is insoluble in cold water, slightly soluble in hot water or alcohol, and dissolves readily to a deep blue solution in alkali hydroxides or carbonates; it is readily soluble in concentrated sulphuric acid, forming a brownish-yellow solution which, on addition of water, yields the unchanged acid and not a sulphate. P. H.

Elaterin. JACQUES POLLAK (*Ber.*, 1906, **39**, 3380—3382. Compare Thoms, *Chem. Zeit.*, 1906, 923; Berg, this vol., i, 596).—The analytical data for elaterin agree equally well with Zwenger's formula, $C_{20}H_{28}O_5$, or with that of Berg, $C_{28}H_{38}O_7$. The values obtained for the molecular weight vary considerably. The compound dissolves in alcoholic potash, but is partially decomposed and acetic acid is liberated. The amount of acetic acid produced on hydrolysing with dilute sulphuric acid (11.2 per cent. of acetyl) agrees best with Zwenger's formula. J. J. S.

Elaterin. FRANZ VON HEMMELMAYR (*Ber.*, 1906, **39**, 3652—3653. Compare preceding abstract).—The analytical results obtained for elaterin and its bromo-derivative agree best with the formula $C_{24}H_{34}O_6$.

Elaterin yields a *di-phenylhydrazone*, and when heated with alcoholic sulphuric acid yields acetic acid and a phenol, *elateridin*, $C_{22}H_{32}O_5$. Boiling with potassium hydroxide solution converts elaterin into *elateric acid*. J. J. S.

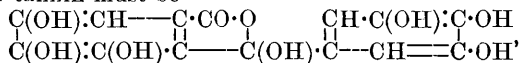
Chlorophyll Absorption. M. TSVETT (*Chem. Centr.*, 1906, ii, 892—893; from *Ber. Deutsch. bot. Ges.*, 1906, **24**, 316—323).—A detailed account of the selective extraction of the various colouring matters in plants by a number of different solvents, together with a description of the method of separating these colouring matters. P. H.

Kamala and Rottlerin. HANS TELLE (*Arch. Pharm.*, 1906, **244**, 441—458. Compare A. G. Perkin, *Trans.*, 1893, **63**, 975; 1895, **67**, 230).—Rottlerin, obtained from a commercial specimen of kamala, melted at 203—204°; the empirical formula $C_{11}H_{10}O_3$ (= 190) and the

molecular weight 486 (determined cryoscopically in naphthalene) were confirmed. When heated for ten minutes with aqueous barium hydroxide solution, saturated in the cold, rottlerin yields 10 to 15 per cent. of phloroglucinol methyl ether, and also resinous substances, whilst some of it is converted into a reddish- or violet-brown isomeride, *ψ-rottlerin*, melting at 235°. When heated for some ten hours with zinc powder and 15 per cent. aqueous sodium hydroxide, rottlerin yields about 60 per cent. of resin and about 30 per cent. of phenols; also a considerable quantity of β -phenylpropionic acid, a little acetic acid, and a small quantity of a crystalline acid which melts at 185—185.5° and contains C 72.4, H 6.4 per cent. From the mixture of phenols, phloroglucinol mono- and di-methyl ethers were isolated. Probably phloroglucinol trimethyl ether was present also, and it was isolated with certainty from a product obtained by using 2 per cent., instead of 15 per cent., aqueous sodium hydroxide; from this product a small quantity of a *substance* melting at 170—172° and smelling like camphor was isolated.

C. F. B.

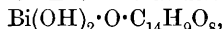
Constitutional Formula of Tannin. Correction. J. DEKKER (*Ber.*, 1906, 39, 3784. Compare this vol., i, 686).—The constitutional formula for tannin must be



and not as previously given.

G. Y.

Preparation of Bismuth Tannate. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 172933).—When bismuth hydroxide is heated with a solution of tannin the well known bismuth subtannate,



is produced; when, however, the interaction is effected at the ordinary temperature the *bismuth ditannate*, $\text{Bi}(\text{OH})(\text{O} \cdot \text{C}_{14}\text{H}_9\text{O}_8)_2$, is obtained. This substance is prepared by adding a solution of bismuth nitrate in dilute nitric acid to a solution of tannin in aqueous sodium carbonate and stirring the mixture for six hours. The product is a pale yellow powder. On boiling with water, the ditannate loses tannic acid and is converted into the monotannate.

G. T. M.

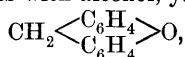
Brominated 4-Pyrones and their Hydroperbromides. FRANZ FEIST) *Ber.*, 1906, 39, 3659—3664. Compare Collie and Tickle, *Trans.*, 1900, 77, 1115; Feist and Baum, *Abstr.*, 1905, i, 914; Hantzsch and Denstorff, this vol., i, 745).—*Ethyl hydrogen dibromochelidonate*, $\text{O} \left\langle \begin{array}{c} \text{C}(\text{CO}_2\text{H})\text{:CBr} \\ \text{C}(\text{CO}_2\text{Et})\text{:CBr} \end{array} \right\rangle \text{CO}$, may be obtained from the mother liquors in the preparation of ethyl dibromochelidonate; it crystallises with $2\text{H}_2\text{O}$ and then melts at 85°, but in the anhydrous state melts at 182—183°.

Sulphuryl chloride reacts with a solution of ethyl acetonedioxalate in dry ether, yielding *ethyl dichlorochelidonate*, $\text{C}_{11}\text{H}_{10}\text{O}_6\text{Cl}_2$, which crystallises from methyl alcohol in glistening prisms melting at 137—138°. A by-product is *ethyl chlorochelidonate*, $\text{C}_{11}\text{H}_{11}\text{O}_6\text{Cl}$, melting at 77°. The separation of the mono- and di-chloro-derivatives is difficult. Iodine reacts

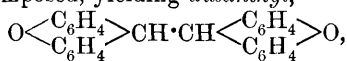
with an acetic acid or acetone solution of ethyl acetonedioxalate, yielding a product free from halogen. It decomposes above 250° , is soluble in alkalis, and its analytical data agree with the formula $C_{14}H_{12}O_{16}$.
J. J. S.

New Reactions of some Hydrols. ROBERT FOSSE (*Bull. Soc. chim.*, 1906, [iii], 35, 1005—1017. Compare this vol., i, 691, 756).—

Xanthydrol, $OH \cdot CH \begin{smallmatrix} \diagup C_6H_4 \\ \diagdown C_6H_4 \end{smallmatrix} O$, condenses with hydroxylamine, forming a *product*, $C_{13}H_{11}O_2N$, which crystallises in needles, and, on treatment with a solution of hydrogen chloride in alcohol, yields hydroxylamine hydrochloride and *xanthyl chloride*, $CH \begin{smallmatrix} \diagup C_6H_4 \\ \diagdown C_6H_4 \end{smallmatrix} OCl$, which is unstable and reacts with alcohol, yielding xanthen,

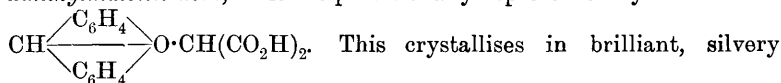


and acetaldehyde. The substance $C_{13}H_{11}O_2N$ begins to melt at 140° and at 150° is decomposed, yielding *dixanthyl*,



which crystallises in needles and melts at 204 — 205° . Xanthydrol also reacts with semicarbazide, yielding a *product*, $C_{14}H_{13}O_2N_3$, which melts and decomposes at 170 — 171° and reacts with hydrogen chloride in alcohol in much the same way as the oxime described above.

With malonic acid in acetic acid, xanthydrol condenses to form *xanthylmalonic acid*, which is provisionally represented by the formula

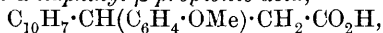


tablets, decomposes at 140° , forming a green liquid, is decomposed by hydrogen bromide in acetic acid, forming *xanthyl bromide* and malonic acid, and by hydrogen chloride in alcohol, yielding xanthen, acetaldehyde and malonic acid. When heated with pyridine, it furnishes xanthylacetic acid, $O \begin{smallmatrix} \diagup C_6H_4 \\ \diagdown C_6H_4 \end{smallmatrix} CH \cdot CH_2 \cdot CO_2H$, which is not attacked by the halogen acids.

Dinaphthapyrylmalonic acid, $CH \begin{smallmatrix} \diagup C_{10}H_6 \\ \diagdown C_{10}H_6 \end{smallmatrix} O \cdot CH(CO_2H)_2$, obtained by the action of malonic acid on dinaphthapyranol or dinaphthapyryl bromide, is decomposed by hydrogen chloride into malonic acid and dinaphthapyryl chloride, and by pyridine into dinaphthapyrylacetic acid and carbon dioxide.

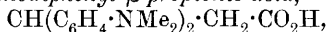
Xanthylecyanoacetic acid, similarly obtained, decomposes at 164 — 166° . It is decomposed by hydrogen bromide in acetic acid, yielding xanthyl bromide and cyanoacetic acid, and with pyridine furnishes *xanthylacetoneitrile* which melts at 140° .

p-Methoxyphenyl- α -naphthyl- β -propionic acid,



obtained by condensing malonic acid with *p*-methoxyphenyl- α -naphthyl-carbinol, furnishes a *p-toluidide*, which melts at 176 — 177° . 3 : 4-*Methyl-*

enedioxyphenyl- α -naphthyl- β -propionic acid, prepared similarly, melts at 205°. *p*-Dimethylaminophenyl- α -naphthyl- β -propionic acid melts at 183°. *pp*-Tetramethyldiaminodiphenyl- β -propionic acid,



obtained from Michler's hydrol, melts at 222°. Triphenylcarbinol, when fused with malonic acid, yields triphenyl- β -propionic acid. Cyanoacetic acid condenses with *p*-methoxyphenyl- α -naphthylcarbinol to form an acid, $\text{C}_{21}\text{H}_{17}\text{O}_3$, and a similar product is obtained on condensation with Michler's hydrol. Triphenylcarbinol and cyanoacetic acid gives (1) a product, $\text{C}_{22}\text{H}_{17}\text{O}_2\text{N}$, which crystallises in colourless needles and melts and decomposes at 155°, and (2) a neutral, nitrogenous substance which melts at 114–115°. Benzhydrol reacts with cyanoacetic acid to form a nitrogenous compound, insoluble in acids, which melts at 144–155°.

[With N. ROBYN.]—A large number of inorganic salts of the above acids have been prepared and analysed. The condensation products of these with β -ketonic esters (this vol., i, 756), when heated with acetic acid in a closed tube, yield ketones, thus ethyl xanthylacetoacetate furnishes *xanthylpropanone*, $\text{O} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{COMe}$, which crystallises from light petroleum in slender needles and melts at 101–102°. *Xanthylacetophenone*, similarly obtained from ethyl xanthylbenzoylacetate, forms small, white crystals and melts at 83–84°.

[With M. BAILLON.]—*Xanthylacetanilide* forms long, silky needles and melts at 213–214°. *Xanthylaceto-o-toluidide* crystallises in slender needles and melts at 215–216°; the *meta*-isomeride melts at 153–154°, and the *para*-compound at 204–205°. *Xanthylaceto- α -naphthalide* melts at 210–211°, and the β -isomeride at 225–216°.

T. A. H.

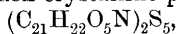
Alkaloids of Calumba Root. JOHANNES GADAMER (*Arch. Pharm.*, 1906, 244, 255–256. Compare Abstr., 1903, i, 50).—An introduction to the following paper, and to one by K. Feist that will appear shortly.

C. F. B.

Alkaloids of Calumba Root. E. GÜNZEL (*Arch. Pharm.*, 1906, 244, 257–269. Compare Gadamer, Abstr., 1903, i, 50).—From an alcoholic extract of the root the alcohol was distilled; the residue was diluted with a little water and much alcohol; ether was added, producing a viscid precipitate; the solution was filtered and evaporated, and the residue dissolved in water and shaken with ether, which dissolved fatty substances and columbine. The aqueous liquid was freed from alcohol and ether by heating, clarified with kieselguhr, and precipitated with potassium iodide; from the precipitate the *iodide* melting at 210°, of an alkaloid “B” was extracted by boiling with alcohol, and columbamine iodide remained.

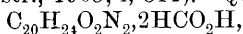
Columbamine iodide, probably, $\text{C}_{21}\text{H}_{22}\text{O}_5\text{NI} = \text{C}_{17}\text{H}_{10}\text{ONI}(\text{OMe})_4$, is yellow and melts at 224°; the corresponding *chloride* crystallises with $2\frac{1}{2}\text{H}_2\text{O}$ in yellow needles melting at 194°, and with $4\text{H}_2\text{O}$ in brown prisms melting at 184°; the *hydrogen sulphate* melts at 220–222°; a

crystalline aurichloride, platinichloride, and nitrate were prepared but not analysed; a greenish-black crystalline pentasulphide,



melting at 139° , was obtained from the iodide by the action of yellow aqueous ammonium sulphide (compare Schreiber, *Arch. Pharm.*, 1890, 228, 631; Abstr., 1890, 1012). The iodide is reduced in aqueous solution by zinc and sulphuric acid to the iodide of a base $\text{C}_{21}\text{H}_{25}\text{O}_5\text{N} = \text{C}_{17}\text{H}_{13}\text{ON}(\text{OMe})_3$, *tetrahydrocolumbine*, which melts at 142° and is sensitive to light and air; the *platinichloride* of this mono-acid base melts at 228° ; the chloride and aurichloride, the latter melting at 201° , were prepared but not analysed. C. F. B.

Quinine Formates. P. GUIGUES (*J. Pharm. Chim.*, 1906, [vi], 24, 301—302. Compare Abstr., 1905, i, 811).—*Quinine formate*,



obtained by neutralising a solution of quinine or quinine sulphate in excess of dilute formic acid with ammonia solution, is very soluble in water, melts below 100° , and loses some formic acid.

A *basic quinine formate*, $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2 \cdot \text{HCO}_2\text{H}$, is obtained by dissolving quinine in the requisite quantity of formic acid and adding ammonium formate to the solution. This does not decompose when heated at 100° and dissolves in less than 20 parts of water. T. A. H.

New Salt of Quinine. LUIGI SANTI (*Chem. Centr.*, 1906, ii, 1205—1206; from *Boll. Chim. Farm.*, 1906, 45, 557—560).—On mixing together ethereal solutions of pure quinine, $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2 \cdot 3\text{H}_2\text{O}$, and of acetylsalicylic acid and leaving the mixture for twelve hours, a quantitative yield of a salt is obtained which has the composition $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H} \cdot \text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2$. This substance which is insoluble in ether but dissolves readily in alcohol or chloroform melts at 157° . P. H.

Thioquinine and Thiocinchonine. EZIO COMANDUCCI and LUIGI PESCIATELLI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 280—285).—*Thioquinine*, $(\text{C}_{20}\text{H}_{23}(\text{ON})_2)_2\text{S}$, prepared by the action of phosphorus pentasulphide on quinine in chloroform solution, separates from alcohol as a yellow, micro-crystalline powder melting at 150 — 152° and is soluble in chloroform and sparingly so in ether. It has an odour resembling that of onions and it dissolves in nitric or sulphuric acid, giving a blue fluorescence. With chlorine or bromine water and ammonia it gives the thalleioquinine reaction, and with chlorine water, potassium ferrocyanide, and ammonia it yields a red coloration. When dissolved in dilute sulphuric acid and treated with acetic acid, alcohol, and tincture of iodine, it gives the herapathite reaction. In boiling chloroform solution, it has the normal molecular weight.

Thiocinchonine, $(\text{C}_{19}\text{H}_{21}\text{N}_2)_2\text{S}$, prepared by the action of phosphorus pentasulphide on cinchonine, is deposited from alcohol as an amorphous powder having an odour like that of garlic, and decomposes, without melting, at about 130° . It dissolves in chloroform, in which it exhibits normal ebullioscopic behaviour, and, to a slight extent, in ether.

T. H. P.

Extraction of Coca Leaves. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1906, **25**, 311—329. Compare Abstr., 1905, ii, 778; this vol., ii, 315, 625).—In the industrial process for the extraction of the alkaloids from Peruvian coca leaves, the leaves in a fine state of division are treated with a mixture of dilute sodium carbonate solution and petroleum, the petroleum solution of the alkaloids is then neutralised with dilute hydrochloric acid, and the aqueous solution of the hydrochlorides of the alkaloids decomposed by sodium carbonate and the alkaloids extracted by petroleum. The author finds that the best results are obtained when ammonia is used instead of sodium carbonate, and ether instead of petroleum in the above method of extraction; from an exhaustive series of experiments (for details of which the original must be consulted) it is shown that the percentage of the total alkaloid extracted depends on: (1) the action of excess of sodium carbonate, ammonia, or hydrochloric acid on the alkaloids, (2) the solubility of the alkaloids in the petroleum, (3) the quantities of sodium carbonate and of water, (4) the quantity of petroleum and the duration of the extraction, (5) the state of division of the leaves, and (6) the quantities of hydrochloric acid and sodium carbonate or ammonia employed in the last stage of the process. Comparative experiments conducted on fresh leaves and dried leaves showed that whilst 3 kilos. of the fresh leaves yielded 6.65 grams of alkaloids, the same weight of leaves after drying yielded 10.65 grams. M. A. W.

Ephedrine and ψ -Ephedrine. ERNST SCHMIDT and HERMANN EMDE (*Arch. Pharm.*, 1906, **244**, 241—255).— ψ -Ephedrine, obtained from ephedrine (E. Schmidt, this vol., i, 602), was found to be identical with the natural base in rotation ($[\alpha]_D$ 51.2° at 20°, in 0.5 per cent. alcoholic solution) and crystalline form (rhombic system; $a:b:c=0.843:1:1.858$). Ephedrine undergoes a partial transformation when it is heated by itself at 100°, or with aqueous sodium carbonate.

When ψ -ephedrine is heated with methyl-alcoholic methyl iodide it is converted partially into oily *methyl- ψ -ephedrine*, the *aurichloride* of which, $C_{11}H_{17}ON, HAuCl_4$, melts at 119—123°. When excess of methyl iodide is used, the quaternary *methiodide*, $C_{12}H_{20}ONI$, melting at 205°, is obtained in addition; the corresponding quaternary *aurichloride* and *platinichloride* melt at 194—195° and 204—205° respectively. These salts differ distinctly, although often only slightly, from the corresponding salts derived from ephedrine; and the quaternary iodide crystallises in the rhombic system ($a:b:c=0.642:1:1.209$) whilst the quaternary iodide from ephedrine is rhombic with sphenoidal hemihedry ($a:b:c=0.979:1:0.761$); again, ψ -ephedrine hydriodide, melting at 172°, is rhombic and holohedral ($a:b:c=0.603:1:1.372$), whilst ephedrine hydriodide, melting at 155—156°, although rhombic, is hemihedral (0.737:1:0.286).

Methyl- ψ -ephedrine methyl hydroxide, when subjected to prolonged distillation with water, decomposes into trimethylamine and an unsaturated substance, $C_9H_{10}O$, which boils at 197—199°. A similar result is obtained with methylephedrine methyl hydroxide, except that the unsaturated substance boils at 212—216°, and possibly is identical with α -phenylallyl alcohol, $CH_2:CH \cdot CHPh \cdot OH$.

A formula suggested as possible for ephedrine is
 $\text{NHMe} \cdot \text{CHMe} \cdot \text{CHPh} \cdot \text{OH}$.

C. F. B.

Ergot. FRIEDRICH KRAFFT (*Arch. Pharm.*, 1906, **244**, 336—359).—The following substances were isolated: A phytosterol: ergosterol (Tanret). Two alkaloids: ergotinine (Tanret; Keller's "cornutine" and Jakobi's "secaline"); and *hydroergotinine*, which is isomorphous and more soluble. A crystalline δ -lactonic acid, *secalonic acid*, $\text{C}_{14}\text{H}_{14}\text{O}_6$, which is yellow and melts at 244° ; and the corresponding *hydroxy-acid*, and another *acid* formed by loss of carbon dioxide, both of which are yellow and amorphous. *Aminosecalesulphonic acid* (Kobert's "ergotic acid"), $\text{NH}_2 \cdot \text{C}_{15}\text{H}_{27}\text{O}_{15} \cdot \text{SO}_3\text{H}$. Betaine, choline and manitol.

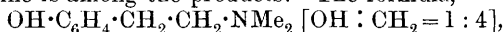
The alkaloids are poisons, causing convulsions and gangrene, but they do not cause the specific action of the drug on the uterus.

C. F. B.

Ergotinine. CHARLES TANRET (*J. Pharm. Chim.*, 1906, [vi], **24**, 397—403).—Since ergotinine combines with phenol, the use of the latter as a solvent for cryoscopic determinations of the molecular weight of ergotinine is not permissible (see Barger and Carr, *Pharm. J.*, 1906, [iv], **23**, 257). From the analysis of its salts, the formula $\text{C}_{35}\text{H}_{40}\text{O}_5\text{N}_5$ is deduced. The use of the name ergotoxine, applied by Barger and Carr (*loc. cit.*) to amorphous ergotinine, is objected to.

E. F. A.

Hordenine. OTTO GAEBEL (*Arch. Pharm.*, 1906, **244**, 435—441. Compare Léger, this vol., i, 204, 761).—Hordenine, $\text{C}_{10}\text{H}_{15}\text{ON}$, is oxidised completely by permanganate. If it is methylated by shaking a solution of it in aqueous potassium hydroxide with dimethyl sulphate, and the resulting alkaline solution oxidised with potassium permanganate on the water-bath, anisic acid is obtained. When the methiodide is treated with silver hydroxide, and the quaternary ammonium hydroxide which results is submitted to dry-distillation, trimethylamine is among the products. The formula,



is the only one which expresses these reactions of hordenine satisfactorily.

C. F. B.

Alkaloids of Tobacco. AMÉ PICTET (*Arch. Pharm.*, 1906, **244**, 375—389).—A complete account of researches already published (Abstr., 1895, i, 627; 1898, i, 50, 688; 1899, i, 164; 1900, i, 685; 1901, i, 339; 1904, i, 86, 520, 771; 1905, i, 545, 543).

The subjects dealt with are:—Constitution of nicotine; synthesis of nicotine; nicotine; nicotene; nicotimine; nicotelline; pyrrolidine.

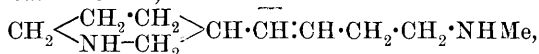
C. F. B.

Opium Alkaloids and the Constitution of Berberine and Morphine. FRANZ FALTIS (*Chem. Centr.*, 1906, ii, 1011—1012; from *Pharm. Post*, **39**, 497—499).—The author discusses the common origin of the alkaloids papaverine, narcotine, berberine, corydaline, morphine, codeine, thebaine, protopine, glaucine, and chelidoneine, and arrives at conclusions different from those of Perkin, Pschorr, and Freund as to the formulæ of berberine and morphine.

P. H.

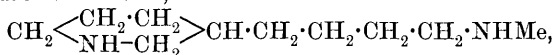
Reduction of Metanictine with Sodium and Absolute Alcohol. II. EMIL MAAS and ADOLF HILDEBRANDT (*Ber.*, 1906, 39, 3697—3702. Compare *Abstr.*, 1905, i, 543).—The product, obtained by reducing metanictine by means of sodium and absolute alcohol, is not uniform, but a mixture of hexahydrometanictine and octahydrometanictine, which may be separated by fractional distillation in a current of steam.

Hexahydrometanictine,



is an oil which boils at 248—250°, has the sp. gr. 0.9578 at 20°/4°, and is volatile with steam. It is optically inactive. The *platinichloride*, $\text{C}_{10}\text{H}_{20}\text{N}_2 \cdot \text{H}_2\text{PtCl}_6$, melts and decomposes at 225°.

Octahydrometanictine,



is an oil which boils at 258.5—260°; it is also volatile with steam. It has the sp. gr. 0.9173° at 20°/4°, and is optically inactive. Its *hydrochloride*, $\text{C}_{10}\text{H}_{22}\text{N}_2 \cdot 2\text{HCl}$, separates from water in glistening, colourless needles and melts at 202°; the *platinichloride*,



melts and decomposes at 202.5°; the *aurichloride*, $\text{C}_{10}\text{H}_{22}\text{N}_2 \cdot 2\text{HAuCl}_4$, melts at 142°.

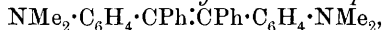
A. McK.

Solanine Extracted from Solanum sodomæum. GIUSEPPE ODDO and AMEDEO COLOMBANO (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 312—319. Compare this vol., i, 527).—The melting point of solanine varies considerably with the size of the flame by which it is heated, so that it cannot be used as a criterion of purity.

The authors have effected greater purification of solanine by crystallising it several times from 80 per cent. alcohol, then dissolving it in very dilute sulphuric acid, filtering, precipitating by means of alcohol sodium hydroxide and washing with water until all the alkali is removed. After repetition of this process and further crystallisation from alcohol, the solanine obtained gives, on analysis and molecular weight determination in acetic acid, numbers agreeing well with the formula $\text{C}_{27}\text{H}_{47}\text{O}_9\text{N}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$.

T. H. P.

Amino-derivatives of Tetraphenylethylene. Quinonoid Compounds. X. RICHARD WILLSTÄTTER and MAX GOLDMANN (*Ber.*, 1906, 39, 3765—3776).—s-4 : 4'-*Tetramethyldiaminotetraphenylethylene*,



prepared by reduction of *p*-dimethylaminobenzophenone with tin and hydrochloric acid in alcoholic solution, crystallises on addition of ether or light petroleum to its solution in benzene or chloroform in long, glistening, lemon-yellow needles, melts at 224—225°, decomposes above 300°, and gives a deep-red coloration with ferric chloride in acid solutions. The *hydrochloride* and *sulphate* form colourless needles, the dark reddish-brown *mercurichloride* and *platinichloride* are insoluble.

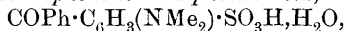
When reduced by means of zinc dust in glacial acetic acid solution, *p*-dimethylaminobenzophenone yields s-4 : 4'-*tetramethyldiaminotetraphenylethyleneglycol*, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}(\text{OH}) \cdot \text{CPh}(\text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, which crys-

tallises in slender spears, melts and decomposes at 186—187°, becomes yellow on exposure to light, and dissolves in concentrated hydrochloric acid, forming a colourless solution which becomes red slowly at the ordinary temperature or more quickly when heated. When reduced with zinc dust and glacial acetic acid, the pinacone yields tetramethyldiaminotetraphenylethylene and a *substance*, which is obtained also by the action of concentrated sulphuric acid on the pinacone, crystallises in colourless, rhombic and octagonal leaflets, melts at 255—256°, has feeble basic properties, and does not give a coloration with ferric chloride in acid solutions.

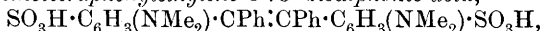
When boiled with absolute alcohol, the pinacone yields a *pinacoline*, $C_{30}H_{30}ON_2$, which crystallises in rhombic plates, melts at about 214—217°, and forms a *hydrochloride* crystallising in long, silky, hexagonal leaflets.

p-Dimethylaminobenzylhydrol ethyl ether, $NMe_2 \cdot C_6H_4 \cdot CHPh \cdot OEt$, prepared by the action of alcohol on the benzhydrol in presence of an acid, crystallises in colourless needles, melts at 37—37·5°, boils at 206—208° under 14 mm. pressure, has a slight odour of benzaldehyde, and gives with hot concentrated hydrochloric acid an intense yellow, with concentrated sulphuric acid an intense red, coloration.

4-Dimethylaminobenzophenone-3-sulphonic acid,



formed by the action of fuming sulphuric acid on the ketone at 130°, separates in large, clear, triclinic crystals [$a : b : c = 1.1310 : 1 : 2.8296$; $\alpha = 89^\circ 1'5''$, $\beta = 83^\circ 40'$, $\gamma = 77^\circ 31'$], loses H_2O over sulphuric acid, melts and decomposes at 296—298°, forms yellow solutions, has a strong acid reaction, reduces hot ammoniacal silver solution, and decolorises potassium permanganate in alkaline or acid solution. The *barium*, *calcium*, and *silver* salts are described. The *oxime*, $C_{15}H_{16}O_4N_2S$, crystallises in glistening, white needles, effloresces on exposure to air, and melts and decomposes at 296—298°. When reduced with tin and concentrated hydrochloric acid, the sulphonic acid yields *s*-4 : 4'-tetramethyldiaminotetraphenylethylene-3 : 3'-disulphonic acid,



which is purified by recrystallisation of its *calcium* salt. The acid crystallises in two modifications: in colourless, rhombic plates or leaflets containing $2H_2O$ on slow cooling of the aqueous solution; and in long, white needles on rapid separation from the solution. The latter form effloresces on exposure to air. With acid or neutral oxidising agents the disulphonic acid gives an intense blood-red coloration which is destroyed by reducing agents or alkali hydroxides. The *salts* are yellow.

Reduction of Michler's ketone with tin and concentrated hydrochloric acid leads to the formation of octamethyltetra-aminotetraphenylethylene (Gattermann, Abstr., 1896, i, 172). G. Y.

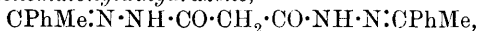
Condensation Products of the Dihydrazides of Dibasic Acids.

CARL BÜLOW and R. WEIDLICH (*Ber.*, 1906, 39, 3372—3377).—*Ethyl malonyl-bis*-[1-amino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate],

$CH_2(CO \cdot NH \cdot N < \begin{smallmatrix} CMe : C \cdot CO_2Et \\ CMe : C \cdot CO_2Et \end{smallmatrix})_2$, prepared by the interaction of

malonyldihydrazide and ethyl diacetylsuccinate in glacial acetic acid solution, crystallises in bundles of needles melting at 122°. *Malonyldiacetyldihydrazide*, $C_7H_{12}O_4N_4$, is a white powder melting at 228°.

Diacetophenonemalonyldihydrazone,

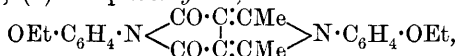


prepared from malonyldihydrazide and acetophenone, melts at 221°; *methyl malonyldihydrazide* melts at 179°, and condenses with ethyl diacetylsuccinate to form *ethyl methylmalonyl-bis-[1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate]* melting at 139—140°. *Dibenzaldehyde methylmalonyldihydrazone* melts at 249°, *methyl malonyldiacetyldihydrazide* at 225°. Succinyldihydrazide melts at 166° (compare Curtius, Abstr., 1895, i, 263), the *diacetyl* derivative at 233°. *Ethyl succinyl-bis-[1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate]* melts at 173°.

E. F. A.

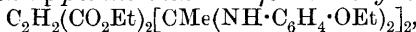
Action of Ethyl Acetylsuccinate and Diacetylsuccinate on Phenetidine. LUCIANO ROSSI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 299—308).—When phenetidine reacts with ethyl acetylsuccinate or diacetylsuccinate, the ketonic group of the latter enters into reaction more readily than the carboxyl group, a fact which indicates that these compounds have the enolic structure.

The interaction of ethyl diacetylsuccinate (1 mol.) and phenetidine (1 mol.) yields: (1) *ethyl 1-p-ethoxyphenyl-2:5-dimethylpyrrole-3:4-dicarboxylate*, $OEt \cdot C_6H_4 \cdot N < \begin{smallmatrix} CMe : C \cdot CO_2Et \\ CMe : C \cdot CO_2Et \end{smallmatrix}$, which crystallises from alcohol in microscopic, yellow prisms and from acetic acid or benzene in stellar aggregates of needles melting at 155—156°; it has a neutral reaction, dissolves in ether, acetone, or ethyl acetate, gives the pyrrole reaction, and, when dissolved in alcohol, yields an intense blue coloration with ferric chloride; (2) the *p-ethoxyanil*,



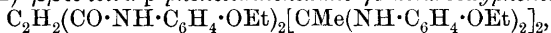
of the foregoing acid; this crystallises from alcohol in tufts of minute, faintly yellow needles melting at 272°, and dissolves sparingly in ether, acetone, benzene, acetic acid, or ethyl acetate; it is a neutral substance and gives the pyrrole reaction, but yields no coloration with ferric chloride.

The interaction of 1 mol. of ethyl diacetylsuccinate and 2 mols. of phenetidine yields: (1) the compound melting at 272° (*vide supra*) (2) *Ethyl ββεε-tetra-p-phenetidinoheptane-γδ-dicarboxylate*,



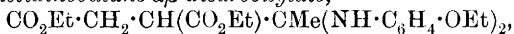
which separates from alcohol as a yellow, microcrystalline powder melting at 159—160°, dissolves sparingly in ether, acetone, benzene, ethyl acetate, or acetic acid, and has a neutral reaction.

The action of 1 mol. of ethyl diacetylsuccinate on 4 or 6 mols. of phenetidine yields: (1) the compound melting at 159—160° (*vide supra*); (2) *ββεε-tetra-p-phenetidinoheptane-γδ-dicarboxyphenetidine*,



which crystallises from alcohol in white needles melting at 230°, dissolves moderately readily in acetone and sparingly in ether, benzene, ethyl acetate, or acetic acid, and has a neutral reaction.

The action of ethyl acetylsuccinate on phenetidine yields: (1) *ethyl γγ-di-p-phenetidinobutane-αβ-dicarboxylate*,



which separates from alcohol in white crystals melting at 114—115°, dissolves in benzene, acetone, or acetic acid, has a neutral reaction, and in cold alcoholic solution gives a green coloration with ferric chloride;

(2) *γγ-Diphenetidinobutane-αβ-dicarboxyphenetidine*,

$\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}(\text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}) \cdot \text{CMe}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt})_2$, which separates from alcohol in white crystals melting at 230—232°, dissolves sparingly in benzene, acetic acid, or ethyl acetate, and has a neutral reaction.

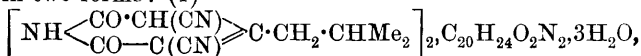
T. H. P.

New Acid of the Tetrahydropyridine Series (2-Oxy-1 : 6 : 6-trimethyl-Δ³-tetrahydropyridine-4-carboxylic Acid). GALEAZZO PICCININI (*Atti R. Accad. Sci. Torino*, 1906, **41**, 1019—1043). —2-Oxy-1 : 6 : 6-trimethyl-Δ³-tetrahydropyridine-4-carboxylic acid,

$\text{NMe} \left\langle \begin{array}{c} \text{CO} - \text{CH} \\ \text{CMe}_2 \cdot \text{CH}_2 \end{array} \right\rangle \text{C} \cdot \text{CO}_2\text{H}$, prepared by the action of permanganate on 3-cyano-1 : 4 : 6 : 6-tetramethylpyridone in neutral solution, crystallises from water in colourless or pale rose-coloured, striated prisms melting at 174—174·5° (corr.), has the normal molecular weight in boiling acetone, and dissolves readily in alcohol, benzene, ethyl acetate, acetic acid, or chloroform, and sparingly in ether. It behaves as a monobasic acid towards alkali hydroxides or carbonates, and, when heated at 290—300°, it evolves methane. It dissolves unchanged in concentrated hydrochloric, sulphuric, or nitric acid, and in aqueous solution it hydrolyses sucrose. It gives with even very dilute ferric chloride solutions an intense blood-red coloration; with dilute ferrous sulphate solution an intense blood-red coloration. The *sodium* (+ H₂O) and *barium* salts of the acid were analysed. The 3 : 5-dibromo-derivative, C₉H₁₁O₃NBr₂, separates from benzene in colourless, prismatic crystals melting at 137—139°, dissolves slightly in water and gives no red coloration with ferric chloride. The isomeric 5 : 5-dibromo-derivative crystallises from benzene with $\frac{1}{2}\text{C}_6\text{H}_6$ in hard, heavy prisms, which effloresce in the air and melt at 201—202°, and its aqueous solution gives a blood-red coloration with ferric chloride; it dissolves readily in alcohol, ether, chloroform, or benzene, and sparingly in carbon disulphide or water, and on heating at its melting point or on boiling with water it loses all its bromine, in the latter case as hydrogen bromide. When heated with potassium hydroxide at 300—320° under a pressure of 40 mm., the acid decomposes, yielding methylamine, oxalic acid, a neutral substance, a syrupy nitrogenous acid, and acrylic acid (?).

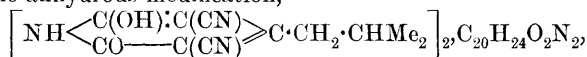
T. H. P.

Transformations of the Quinine Salt of isoButyldicyanoglutaconimide. SILVIO ZUBLENA (*Atti R. Accad. Sci. Torino*, 1906, **41**, 1044—1053).—The quinine salt of isobutyldicyanoglutaconimide exists in two forms: (1)



which crystallises from water in tufts of concentrically-arranged, intensely yellow, slender prisms, and melts and decomposes at about

282°. If this salt, in either the hydrated or the dehydrated form, is suspended in water, it gradually changes into (2) a more stable and less soluble anhydrous modification,



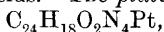
which separates in colourless, probably triclinic, microscopic prisms. This change is accelerated by the action of light. The colourless modification begins to turn yellow at 200°, and, like the yellow form, melts and decomposes at about 282°. A solution of the colourless salt in 60 or 95 per cent. alcohol deposits the yellow modification.

T. H. P.

Dioximes and similar Compounds. LEO TSCHUGAEFF (*Ber.*, 1906, **39**, 3382—3389; *J. Russ. Phys. Chem. Soc.*, 1906, **38**, i, 7—9. Compare Abstr., 1905, i, 743).—The behaviour of different metallic solutions towards the stereoisomeric oximes derived from 2-benzoylpyridine and the oxime of 4-benzoylpyridine (Tschtischibabin, Abstr., 1902, i, 175) has been investigated. The only oxime which give colorations or precipitates is the 2-benzoylpyridineoxime melting at 150—152°, and hence the *syn*-configuration, $\text{C}_5\text{NH}_5 \cdot \text{C} \cdot \text{Ph}$, is assigned

$$\text{HO} \cdot \text{N} \cdot$$
to it.

The *palladium* compound, $\text{C}_{24}\text{H}_{18}\text{O}_2\text{N}_4\text{Pd}$, obtained by the action of palladium ammonium chloride on an alcoholic solution of the oxime, crystallises in canary-yellow needles, sparingly soluble in alcohol or ether. It may be recrystallised from chloroform, and is not decomposed by dilute alkalis or weak acids. The *platinum* derivative,



prepared by the action of platinum pyridine chloride on the oxime, forms dark yellow crystals.

Thiele's nitrosoguanidine, represented by the tautomeric formula $\text{NH}:\text{C}(\text{NH}_2)\text{N}:\text{N} \cdot \text{OH}$, also yields metallic derivatives. Structural formulæ for the metallic compounds are given. J. J. S.

Quinoline Derivatives. II. Nitration of Quinoline and its Mononitro-derivatives. ADOLF KAUFMANN and HERMAN DECKER (*Ber.*, 1906, **39**, 3648—3651. Compare Claus and Kramer, Abstr., 1885, 908; Claus and Hartmann, Abstr., 1896, i, 391; Claus and Schnell, *ibid.*, 319).—6-Nitroquinoline may be further nitrated when heated with the theoretical amount of potassium nitrate and concentrated sulphuric acid at 130—140° for ten hours. The product is a mixture of 5:8-dinitroquinoline and an isomeric compound melting at 185°. The latter dissolves readily in most organic solvents and in dilute sodium hydroxide solution; it does not react with methyl iodide and is readily sublimed.

7-Nitroquinoline is readily nitrated when heated with fuming nitric and concentrated sulphuric acid, the chief product being a new dinitroquinoline melting at 225°. It sublimes readily and dissolves in sodium hydroxide to a characteristic yellow solution. A second product is a dinitro-compound melting at 175°, probably identical with 5:7-dinitroquinoline.

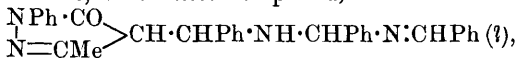
8-Nitroquinoline when boiled for twenty hours with a mixture of

nitric and sulphuric acid, yields 6:8-dinitroquinoline, identical with the product obtained from 2:4-dinitroaniline (La Coste, Abstr., 1882, 979). J. J. S.

Diphenylhydrazones of a Series of Aldehydes. A. D. MAUREN-BRECHER (*Ber.*, 1906, **39**, 3583—3587. Compare Clowes and Tollens, Abstr., 1900, ii, 56).—The *diphenylhydrazones* of the following aldehydes are described; the formulæ and crystalline forms are those of the hydrazones; the temperatures are melting points. Formaldehyde, $C_{13}H_{12}N_2$, white plates, 34·5—35°; propaldehyde, $C_{15}H_{16}N_2$, long, white needles, 20—21°; butaldehyde, $C_{16}H_{18}N_2$, oil; isobutaldehyde, white plates, 30—30·5°; isovaleraldehyde, $C_{17}H_{20}N_2$, white plates or prisms, 36—36·5°; *o*-tolualdehyde, $C_{20}H_{18}N_2$, white needles, 103—104°; *m*-tolualdehyde, light yellow plates, 74—75°; *p*-tolualdehyde, white needles, 83—84°; cinnamaldehyde, $C_{21}H_{18}N_2$, yellow needles, 135—136°; cuminaldehyde, $C_{22}H_{22}N_2$, yellow needles, 78·5—79·5°; *o*-hydroxybenzaldehyde, $C_{19}H_{16}ON_2$, colourless needles, 138·5°; *m*-hydroxybenzaldehyde, yellow needles, 118—119°; vanillin, $C_{20}H_{18}O_2N_2$, violet leaflets, 130—131°; piperonal, $C_{20}H_{16}O_2N_2$, white plates, 134—135°. G. Y.

Spontaneous Oxidation in presence of Benzaldehyde. MARIO BETTI (*Gazzetta*, 1906, **36**, ii, 427—433).—When dissolved in alcoholic ammonia in presence of a few drops of benzaldehyde or hydrogen peroxide or sodium peroxide, 1-phenyl-3-methyl-5-pyrazolone undergoes oxidation, yielding: (1) rubazonic acid; (2) 1-phenyl-4-benzylidene-3-methyl-5-pyrazolone; (3) 4-benzylidene-bis-1-phenyl-3-methyl-5-pyrazolone, $CHPh\left(\begin{array}{c} CO-NPh \\ \diagup \\ CMe:N \end{array}\right)_2$, which separates in shining, white crystals melting at 167°; the formation of this compound, together with benzaldehyde, from 1-phenyl-4-benzylidene-3-methyl-5-pyrazolone (2 mols.) and water is a reversible reaction. Whether the function of the benzaldehyde in the above reaction is merely to form hydrogen peroxide or some other peroxide or whether it takes part in a cycle of changes, at the end of which it is regenerated, is yet undecided.

On mixing alcoholic solutions of hydrobenzamide and 1-phenyl-3-methyl-5-pyrazolone, an *additive* compound,



is formed in shining, white prisms which turn yellow at 110° and melt and decompose at 125—126°. This compound may also be used in place of benzaldehyde for the oxidation of 1-phenyl-3-methyl-5-pyrazolone. T. H. P.

New Additive Compounds of 1-Phenyl-2:3-dimethylpyrazolone (Antipyrine). FELICE GARELLI and G. A. BARBIERI (*Gazzetta*, 1906, **36**, ii, 168—172).—Contrary to Schuyten's statement (Abstr., 1898, i, 92, 452), an aqueous solution of the additive compound of antipyrine with zinc chloride gives a precipitate of zinc sulphide with ammonium sulphide. Solutions of the compounds formed by anti-

pyrine with mercuric chloride, bromide, and cyanide give the same reactions as solutions of the mercuric haloid salts themselves. With ferric chloride, solutions of all the additive compounds of antipyrine yield the deep red coloration given by solutions of pure antipyrine.

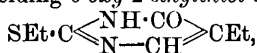
Cryoscopic measurements of various additive compounds of antipyrine in water lead to the following values for the molecular weights, the true values of which are given in brackets: Antipyrine-mercuric cyanide, $\text{Hg}(\text{CN})_2 \cdot \text{C}_{11}\text{H}_{12}\text{ON}_2$, 210—222 (440); antipyrine-quinol, $\text{C}_6\text{H}_4(\text{OH})_2 \cdot 2\text{C}_{11}\text{H}_{12}\text{ON}_2$, 151—171 (487); antipyrine-resorcinol,

$\text{C}_6\text{H}_4(\text{OH})_2 \cdot \text{C}_{11}\text{H}_{12}\text{ON}_2$, 140—151 (298); antipyrine-chloral, $\text{CCl}_3 \cdot \text{CH}(\text{OH})_2 \cdot \text{C}_{11}\text{H}_{12}\text{ON}_2$, 178—183 (352). In aqueous solution, therefore, these compounds are completely resolved into their components.

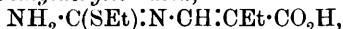
The author is of opinion that the structural formulæ attributed to the double compounds formed by antipyrine have no greater value than the constitutional formulæ proposed for the natural silicates.

T. H. P.

Pyrimidines. XVIII. 5-Ethylcytosine. TREAT B. JOHNSON and GEORGE A. MENGE (*J. Biol. Chem.*, 1906, 2, 105—115. Compare Abstr., 1903, i, 526; this vol., i, 704).—*Ethyl sodioformylbutyrate*, $\text{ONa} \cdot \text{CH} : \text{C} \text{Et} \cdot \text{CO}_2 \text{Et}$, is obtained by the condensation of ethyl formate and ethyl butyrate in the presence of sodium ethoxide. It reacts with ψ -ethylthiocarbamide, yielding 6-oxy-2-ethylthiol-5-ethylpyrimidine,



which crystallises from dilute alcohol in well-developed prisms melting at 119—120°. It dissolves readily in alcohol or benzene, but only sparingly in ether. An intermediate product in its formation is $\beta\psi$ -ethylthiocarbamido- α -ethylacrylic acid,

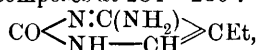


which crystallises in plates melting at 148—149°; at this temperature carbon dioxide is evolved and the pyrimidine derivative formed.

6-Chloro-2-ethylthiol-5-ethylpyrimidine, $\text{C}_8\text{H}_{11}\text{N}_2\text{ClS}$, boils at 160—163° under 24 mm. pressure and is readily converted into the corresponding oxy-derivative. 6-Amino-2-ethylthiol-5-ethylpyrimidine, $\text{C}_8\text{H}_{13}\text{N}_3\text{S}$, obtained by the action of alcoholic ammonia on the chloro-derivative at 130—140°, crystallises from a mixture of benzene and light petroleum in prisms melting at 74—76°.

2 : 6-Dioxy-5-ethylpyrimidine (5-ethyluracil), $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{CH} \end{array} \text{CEt}$, is

obtained by boiling the oxyethylthiol ethyl derivative with hydrobromic acid; it crystallises in microscopic prisms melting and decomposing at about 300°. One gram dissolves in 625 of water at 25°. 5-Ethylcytosine hydrobromide, $\text{C}_6\text{H}_9\text{ON}_3 \cdot \text{HBr}$, obtained by boiling the amino-ethylthiol-ethyl derivative with hydrobromic acid, crystallises in large prisms and melts and decomposes at 284—286°. 5-Ethylcytosine,



crystallises in slender, anhydrous prisms, melts and decomposes at 282—283° and dissolves in about 75 parts of water at 25°. It yields

precipitates with mercuric chloride, phosphotungstic acid and potassium bismuthiodide. The *platinichloride*, $(C_6H_9ON_3)_2 \cdot H_2PtCl_6 \cdot 2H_2O$, dissolves readily in hot water, the *hydrochloride*, $C_6H_9ON_3 \cdot HCl$, crystallises in flat prisms and melts at $238-240^\circ$. The *nitrate* decomposes at $170-172^\circ$, and the *picrate* at $277-278^\circ$. Mixtures of basic hydrobromides have been obtained.

2:6-Dichloropyrimidine (Gabriel, Abstr., 1905, i, 482) may be obtained by heating 2-thiouracil (Wheeler and Bristol, *ibid.*, i, 483) with phosphorus pentachloride. J. J. S.

Preparation of 2-Arylimino-5:5-dialkylbarbituric Acids FARBERWERKE VORM. MEISTER, LUCIUS, and BRÜNING (D.R.-P. 172979).—It has been found that the esters of the dialkylmalonic acids will condense with arylguanidines under the influence of alkali alkoxides in methyl-alcoholic solution, but not in ethyl alcohol.

2-Phenylimino-5:5-diethylbarbituric acid, produced by condensing phenylguanidine nitrate and ethyl diethylmalonate with sodium methoxide in methyl-alcoholic solution, crystallises from acetic acid and melts at 249° .

2-Phenylimino-5:5-dimethylbarbituric acid, prepared in a similar way from methyl dimethylmalonate, crystallises from alcohol in well-defined needles and melts at $249-250^\circ$. 2-p-Tolylimino-5:5-diethylbarbituric acid crystallises in needles and melts at $239-240^\circ$. 2-o-Tolylimino-5:5-diethylbarbituric acid and 2-p-chlorophenylimino-5:5-diethylbarbituric acid melt at 230° and $276-277^\circ$ respectively. These arylimino-derivatives, when hydrolysed with dilute acids, furnish the aromatic amine and the dialkylbarbituric acid. G. T. M.

Preparation of Imino-5:5-dialkylbarbituric Acids. EMANUEL MERCK (D.R.-P. 172980. Compare Abstr., 1905, i, 179).—The imino-dialkylbarbituric acids have already been obtained by condensing carbamide with the esters of cyanodialkylacetic acid in the presence of metallic alkyl oxides. It is now found that the acyl derivatives of carbamide may be employed in this condensation, the condensing agent being sodium alkyl oxide, sodamide, or even metallic sodium.

The sodium derivative, $CO \begin{array}{c} \text{N} \cdot \text{Na} \cdot \text{CO} \\ \text{NH} \cdot \text{C}(\text{NH}) \end{array} > \text{CEt}_2$, of 4-imino-2:6-dioxy-5:5-diethylpyrimidine is obtained by condensing acetylcarbamide with ethyl cyanodiethylacetate in boiling alcoholic sodium ethoxide; the free pyrimidine is set free by acids. This condensation may also be effected by adding the cyanodialkylacetate to an intimate mixture of acetylcarbamide and sodamide suspended in xylene; the reagents are cooled at first, but finally heated at 120° . After removing the xylene, the product, on treatment with water, yields the sodium derivative of the iminodioxymethylpyrimidine. G. T. M.

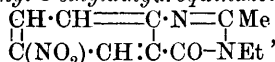
Preparation of 5:5-Dialkylbarbituric Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 173241).—The 4-imino-6-oxy-2-thio-5:5-dialkylpyrimidines, when treated with an oxidising agent,

lose their imino-group and sulphur atom, which are replaced by oxygen, so that a 5:5-dialkylbarbituric acid is produced. It is now shown that this substitution may be effected simply by boiling the thio-compound with an acid; the change occurs in two stages, the imino-group being first removed, and then by further action the sulphur is eliminated. Fuming hydrochloric 40 per cent. sulphuric or 70 per cent. acetic acid may be used for this purpose, and in this way 4-imino-6-oxy-2-thio-5:5-dimethylpyrimidine and its diethyl- and dipropyl-homologues may be transformed into dimethyl-, diethyl-, and dipropyl-barbituric acids respectively. G. T. M.

Quinazolines. XVI. Synthesis of 6-Nitro-4-keto-2-methyl-dihydroquinazolines from 5-Nitroacetylanthranil and Primary Amines. MARSTON T. BOGERT and ELLEN P. COOK (*J. Amer. Chem. Soc.*, 1906, **28**, 1449—1454. Compare this vol., i, 712, and earlier abstracts.)—5-Nitroacetylanthranil, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{C} \begin{smallmatrix} \text{NAc} \\ \text{CO} \end{smallmatrix}$, obtained by the

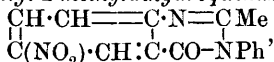
action of acetic anhydride on 5-nitro-acetylanthranilic acid, crystallises in colourless needles and melts at $161\text{--}162^\circ$ (corr.). By the action of dilute aqueous ammonia, it is converted into 6-nitro-4-keto-2-methyl-dihydroquinazoline (6-nitro-4-oxy-2-methylquinazoline), described by Dehoff (Abstr., 1891, 84) and by Thieme (Abstr., 1891, 917). When the anthranil is warmed with methylamine, it is converted into 6-nitro-4-keto-2:3-dimethyldihydroquinazoline (Dehoff and Thieme, *loc. cit.*).

6-Nitro-4-keto-2-methyl-3-ethyldihydroquinazoline,



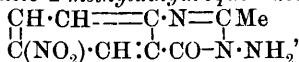
obtained by the action of ethylamine on 5-nitroacetylanthranil, or by the action of ethyl iodide on the sodium derivative of the methylquinazoline, crystallises from alcohol in needles and melts at 166° (corr.).

6-Nitro-4-keto-3-phenyl-2-methyldihydroquinazoline,



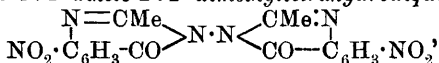
separates from glacial acetic acid in small, pale yellow crystals, melts at $219\text{--}220^\circ$ (corr.), and is sparingly soluble in alcohol.

6-Nitro-3-amino-4-keto-2-methyldihydroquinazoline,



obtained by heating 5-nitroacetylanthranil with hydrazine hydrate in 50 per cent. aqueous solution, crystallises in colourless needles, melts at $208\text{--}209^\circ$ (corr.), and is readily soluble in dilute alcohol. It crystallises from glacial acetic acid with about $2/5$ mol. of acetic acid.

6:6'-Dinitro-4:4'-diketo-2:2'-dimethyltetrahydrodiquinazolyl,

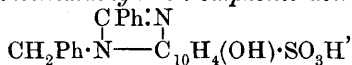


obtained in small yield by heating 5-nitroacetylanthranil (2 mols.) with hydrazine hydrate (1 mol.) in 50 per cent. solution, separates

from glacial acetic acid in small crystals containing 1 mol. of the solvent, and melts and darkens at 281—286°. E. G.

Preparation of 5-Hydroxynaphthabenzaldehyde-7-sulphonic Acid and its Diamino-derivative. LEOPOLD CASSELLA & Co. (D.R.-P. 172931).—1:2-Naphthylenediamine condenses with 2 molecular proportions of benzaldehyde to form naphthabenzaldehyde (Abstr., 1906, i, 536), but the reaction does not take place very readily. If, however, a hydroxysulphonic acid of the diamine is employed, the condensation is easily effected even in aqueous solutions.

5-Hydroxynaphthabenzaldehyde-7-sulphonic acid,



separates completely when benzaldehyde is added to 5:6-diamino- α -naphthol-3-sulphonic acid suspended in water, the mixture being stirred and heated until all the diamino-acid has disappeared. It is a yellow powder which forms a sodium salt crystallising in leaflets.

3':5'-Diamino-5-hydroxynaphthabenzaldehyde-7-sulphonic acid is obtained directly by substituting *m*-aminobenzaldehyde for benzaldehyde in the foregoing condensation, or is obtained by reducing the corresponding nitro-compound obtained by using *m*-nitrobenzaldehyde in the condensation. On diazotising this diamine, a yellow bis-diazo-compound is produced which develops a red coloration with sodium carbonate solution. G. T. M.

Molecular Weight of Indigotin. WILHELM VAUBEL (*Ber.*, 1906, 39, 3587—3588. Compare Abstr., 1901, i, 714; 1902, i, 110).—On recalculating the molecular weight of indigotin as determined cryoscopically in phenol (*loc. cit.*), with the aid of a correction for the maximum solubility of indigotin in the solvent, but with omission of that previously employed for the supposed absorption of water, the author finds his results to be entirely in agreement with those of Beckmann and Gabel (this vol., i, 900). G. Y.

Pyramidone Hydrochloride and Hydrobromide. CHARLES ASTRE and P. AUBOUY (*Bull. Soc. chim.*, 1906, [iii], 35, 856—858).—*Pyramidone hydrochloride*, obtained by mixing a solution of hydrogen chloride in ether with the base dissolved in the same solvent, forms microscopic, colourless, prismatic crystals, melts at 143—144°, and is very hygroscopic, forming a syrupy acid liquid. The *hydrobromide*, similarly obtained, occurs in colourless, microscopic lamellæ, melts at 170—171°, and is very deliquescent, forming an acid liquid.

T. A. H.

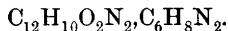
***s*- and *as*-Phenosafraanines.** PHILIPPE BARBIER and PAUL SISLEY (*Bull. Soc. chim.*, 1906, [iii], 35, 858—868. Compare this vol., i, 51).—*s*-Phenosafraanine can be diazotised much more rapidly than *as*-phenosafraanine, and when an aqueous solution of its hydrochloride is shaken with chloroform, the latter does not become coloured as it does when a solution of *as*-phenosafraanine hydrochloride is similarly treated.

These differences in behaviour may be used to distinguish the two dyes.

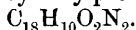
The characters and solubilities of the nitrates and oxalates, and of the hydrates formed by the hydrochlorides and sulphates of the two isomerides, and the conditions under which these salts may be obtained are described in detail in the original. T. A. H.

Azophenols. RICHARD WILLSTÄTTER and MAX BENZ (*Ber.*, 1906, 39, 3492—3503. Compare this vol., i, 997).—This paper contains the results of experiments devised to elucidate a curious case of isomerism among the azophenols. The *p*-azophenol obtained by reducing *p*-benzoquinoneazine differs from the substance prepared by the ordinary methods in its colour in the crystalline and powdered condition, in its behaviour towards moist air, and in its solubility in cold benzene. The new modification is denoted by the affix (α) and the older form by (β). It seems probable that these α - and β -compounds are geometrical isomerides. *p*-Azophenol (α) most conveniently prepared by fusing *p*-nitrophenol with potassium hydroxide, crystallises in a mono-hydrated form from ether or alcohol forming pale brown, or amber-yellow plates with blue reflex. The solubility of the hydrated form in benzene at 17° is 1 in 10,800; the anhydrous form separates from this solvent in cruciform aggregates of greenish-brown crystals. The powdered α -compound assumes a dark yellow colour which becomes green on heating. Both hydrated and anhydrous forms melt and decompose at 215°. A glacial acetic acid solution of hydrogen bromide furnishes blue crystals of the *hydrobromide*, $C_{12}H_{10}N_2 \cdot HBr$.

p-Azophenol (β), prepared by reducing *p*-benzoquinoneazine with phenylhydrazine in benzene solution, forms dark red, and reddish-brown leaflets with a blue reflex; when powdered it is brownish-red with a blue tinge, and at 110—140° it assumes a brick-red colour. The solubility of the β -compound in benzene at 17° is 1 in 1500. On heating a portion of the β -compound under reduced pressure a small yield of the green pulverulent anhydrous α -modification is obtained. The α -compound is partially converted into the β -modification by heating with moist ether. The two isomerides behave similarly towards dry ammonia gas, yielding anhydrous diammonium salts, which completely dissociate in the air or in the desiccator; they are oxidised with equal readiness by silver oxide, and are equally stable towards phenylhydrazine, with which they each combine to form a crystallisable salt,



o-Azophenol, when prepared by the potash fusion method from *o*-nitrophenol is accompanied by a by-product, triphenodioxazine,



The *o*-azo-compound takes up 1 mol. of ammonia to form a coffee-brown ammonium salt; if, however, it has been previously melted or distilled in a vacuum, it does not show any tendency to combine with dry ammonia, but regains the power on recrystallisation or exposure to an atmosphere of damp ammonia. *m*-Azophenol, which combines with a proportion varying between 1 and 2 mols. of ammonia, does not react in ethereal solution with silver oxide.

G. T. M.

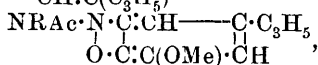
Derivatives of 5-Azoeugenol and the Constitution of the so-called *o*-Hydroxyazo-compounds. GIUSEPPE ODDO and ERNESTO PUXEDDU (*Gazzetta*, 1906, 36, ii, 1—48. Compare Abstr., 1905, i, 492, this vol., i, 774).—After reviewing the present state of knowledge of the hydroxyazo-compounds, the properties of the following azo-compounds derived from eugenol are discussed at some length. The principal conclusions arrived at are as follows.

All the azoeugenols are nearly insoluble in cold 0·5 per cent. aqueous sodium hydroxide, but dissolve much more readily in the same liquid at 100°. No change in the boiling point of the sodium hydroxide solution occurs on adding successive quantities of the azo-compound; this behaviour, which is also shown by phenol and α -naphthol, is held to prove that the azoeugenols yield true sodium salts, which are dissociated to almost the same extent as sodium hydroxide. On cooling the solutions, the sodium salts undergo hydrolysis to the extent of about 58—92 per cent., depending on their structure, the original azoeugenol separating in crystals. No simple connexion can be traced between the degree of hydrolysis of the salts and their solubility. The hydrolysis is held to show that the azoeugenols are pseudo-acids, giving salts only in virtue of a molecular change; they do not redden litmus or combine with ammonia in dry benzene. From their chemical behaviour the free azoeugenols appear to be neither hydrazones nor carbonyl compounds. When boiled with acids or alkalis they do not undergo hydrolysis to form a corresponding quinone; and although they interact vigorously with phenylhydrazine at 110° the product is never a dihydrazone, but always amino Eugenol formed by reduction. Such a reducing action is not observed when ordinary aromatic phenylhydrazones are heated with phenylhydrazine. With hydroxylamine the azoeugenols fail to interact.

The behaviour of the azoeugenols when treated with sodium ethoxide and subsequently with ethyl iodide in alcoholic solution, depends on the nature of the aromatic radicle attached to the azo-group. *o*-Toluenaeugenol, *as-m*-xyleneazoeugenol, and *p*-xyleneazoeugenol do not form ethers; these substances contain a methyl radicle in the ortho-position relatively to the azo-group. Benzeneazoeugenol, *m*-toluenaeugenol, and *p*-bromobenzeneazoeugenol, give unstable ethers which are at once hydrolysed at the ordinary temperature by 0·5 per cent. aqueous sodium hydroxide. Azoeugenols containing negative elements or radicles in any position (with the exception of *p*-bromobenzeneazoeugenol) give well-defined ethers, which are hydrolysed only by warm sodium hydroxide. The ethers differ entirely from the parent azoeugenols in their behaviour with phenylhydrazine; no action occurs at 110° and very little at 170—180°. In no case is amino Eugenol ethyl ether formed. The ethyl ethers of the azoeugenols appear to have the structure, $R \cdot N : N \cdot C \begin{smallmatrix} \text{C(OMe)} \cdot \text{C(OMe)} \\ \text{CH} = \text{C(C}_3\text{H}_5) \end{smallmatrix} \gg \text{CH}$, of true oxygen ethers.

The acetyl derivatives of the azoeugenols are in all cases easily prepared, and are decomposed only slowly by boiling aqueous sodium hydroxide. Like the parent azoeugenols they interact readily with phenylhydrazine at 110—120°, undergoing reduction to amino Eugenol; acetyl amino Eugenol is never formed. The acetyl derivatives thus differ

entirely from the ethyl ethers, and cannot have an analogous structure; the behaviour with phenylhydrazine is moreover held to exclude the structure $\text{NRAc} \cdot \text{N} : \text{C} \begin{matrix} \text{CO} \cdot \text{C}(\text{OMe}) \\ \text{CH} : \text{C}(\text{C}_3\text{H}_5) \end{matrix} > \text{CH}$. The structure



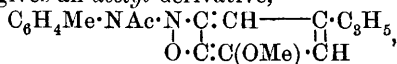
however, is advocated as explaining the properties of the acetyl derivatives.

The parent hydroxyazo-compounds are considered to correspond in structure neither with the alkyl ethers nor with the acetyl derivatives.

The formula, $\text{R} \cdot \text{N} \begin{matrix} \text{H} \\ \text{O} \cdot \text{C} : \text{C}(\text{OMe}) \cdot \text{C} \end{matrix} \begin{matrix} \text{N} \\ \text{C} \cdot \text{CH} \text{---} \text{C} \cdot \text{C}_3\text{H}_5 \end{matrix}$, is attributed to the free

hydroxyazo-compounds, it being assumed that an ordinary single bond can, in certain cases, be divided between two neighbouring elements, as indicated by the sign $<$ in the formula. These compounds are termed *mesohydric* and names such as *benzenemesohydrazoengenol* for benzeneazoenugenol, are given to them.

o-Toluenaeazoenugenol (*o-toluenemesohydrazoengenol*), prepared from the *o*-diazotoluene chloride and sodium eugenoxide (compare Abstr., 1905, i, 492), crystallises from alcohol in dark red, prismatic needles, melts at 92—93°, and gives an *acetyl* derivative,



which crystallises from light petroleum in small, lustrous needles, melts at 72—73°, and is reduced by tin and hydrochloric acid to aminoengenol.

m-Toluenaeazoenugenol forms small, dark red plates, and melts at 79—80°; the *acetyl* derivative forms orange-red needles and melts at 81°; *m-toluenaeazoenugenol ethyl ether* was obtained only as an oil.

p-Toluenaeazoenugenol forms rosettes of dark red needles, melts at 102—103°, and gives an *acetyl* derivative which crystallises in carmine needles and melts at 110—112°; *p-toluenaeazoenugenol ethyl ether* crystallises from dilute alcohol in red prisms or pyramids and melts at 55°.

as-m-Xyleneazoenugenol, prepared from diazotised *as-m*-xylidine, forms red needles and melts at 108°; the *acetyl* derivative forms orange-red needles and melts at 104—105°.

p-Xyleneazoenugenol, prepared from *p*-xylidine, forms reddish-brown crystals and melts at 97°; the *acetyl* derivative melts at 88°.

o-Nitrobenzeneazoenugenol, prepared from diazotised *o*-nitroaniline, crystallises in lustrous, brown spangles or needles, melts at 143°, and gives an *acetyl* derivative which forms dark red needles and melts at 124°; *o-nitrobenzeneazoenugenol ethyl ether* forms orange-red plates and melts at 72—73°. *m-Nitrobenzeneazoenugenol* crystallises from alcohol in needles, melts at 106—107°, and gives an *acetyl* derivative which forms orange-red crystals and melts at 112°; the *ethyl ether* crystallises from alcohol in reddish-orange scales and melts at 86°.

m-Bromobenzeneazoenugenol (*loc. cit.*) melts at 100°, not at 96°, as previously stated; its *ethyl ether* crystallises from alcohol in flattened, orange-red prisms and melts at 100—101°. *p-Chlorobenzeneazoenugenol*

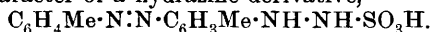
forms rusty-red needles, melts at 117° , and gives an *acetyl* derivative which crystallises in reddish-yellow needles and melts at 113° . *p*-Chlorobenzeneazoeugenol ethyl ether crystallises in silky, reddish-yellow needles and melts at 65° . *p*-Bromobenzeneazoeugenol forms dark-red prisms and melts at 123 — 124° ; the *acetyl* derivative forms orange prisms and melts at 123° . 2:4-Dichlorobenzeneazoeugenol, prepared from 2:4-dichloroaniline, forms rust-coloured crystals and melts at 130° ; the *acetyl* derivative forms reddish-brown needles and melts at 156° . W. A. D.

Action of Sulphurous Acid on Diazo-*m*-toluene Chloride and Sulphate. JULIUS TRÖGER and F. SCHAUB (*Arch. Pharm.*, 1906, 244, 302—307. Compare this vol., i, 120).—In order to obtain the sulphonic acid, $C_{14}H_{16}O_3N_4S$, or $C_6H_4Me \cdot N \cdot N \cdot C_6H_3Me \cdot NH \cdot NH \cdot SO_3H$, in the pure state, the crude acid resulting from the action of sulphur dioxide on an aqueous diazo-*m*-toluene salt should be extracted with boiling water and then dried in a vacuum until constant in weight. Yellow to brown potassium, sodium, ammonium, *aniline*, *p*-toluidine, and *p*-xylidine salts were prepared by adding the acid to concentrated solutions of the acetates of the bases, adding so much water in the first three cases, or alcohol in the last three, that the precipitate dissolves on heating, filtering the solution, and allowing it to crystallise; the last three salts melt and decompose at 151 — 152° , 154° , and 165° respectively. C. F. B.

Action of Sulphurous Acid on Diazobenzene Sulphate. JULIUS TRÖGER and M. FRANKE (*Arch. Pharm.*, 1906, 244, 307—312. Compare this vol., i, 120).—In presence of a large amount of sulphuric acid a diazo-sulphite is formed; when relatively less sulphuric acid is present, the sulphonic acid $C_{12}H_{12}O_3N_4S$, or $NPh \cdot N \cdot C_6H_4 \cdot NH \cdot NH \cdot SO_3H$ is the product; in the presence of still more water, sulphazide, $NHPh \cdot NH \cdot SO_2Ph$, is produced.

The crude sulphonic acid was obtained by diazotising a solution of 15 grams of aniline in 300—500 grams of water and 50 grams of concentrated sulphuric acid, and passing sulphur dioxide into the diazo-solution, kept well cooled. It was purified by adding it to a solution of ammonium acetate, diluting with so much water that the precipitate dissolved on heating, filtering the solution while hot, acidifying with dilute sulphuric acid, and allowing it to cool. The yellow to brown ammonium, *aniline*, *p*-toluidine, and *p*-xylidine salts were prepared in the way described in the preceding abstract; the last three melt and decompose at about 165° , 172° , and 177° respectively. C. F. B.

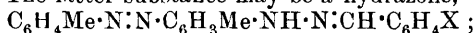
Probable Constitutional Formula of the Sulphonic Acid, $C_{14}H_{16}O_3N_4S$, formed by the Action of SO_2 on Diazo-*m*-toluene. JULIUS TRÖGER, G. WARNECKE, and F. SCHAUB (*Arch. Pharm.*, 1906, 244, 312—325. Compare this vol. i, 120, and preceding abstracts).—The acid has the character of a hydrazine derivative,



Ammoniacal silver and copper solutions convert it, and mercuric oxide

converts its potassium salt, into the *silver*, *ammonium*, and *potassium* salts respectively of an *acid* containing two atoms of hydrogen less in the molecule, $C_6H_4Me \cdot N:N \cdot C_6H_3Me \cdot N:N \cdot SO_3H$; this acid was only obtained as a syrup, which was converted into the *sodium* salt.

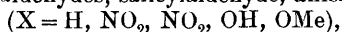
When the first sulphonic acid is treated with an aromatic aldehyde, $C_6H_4X \cdot CHO$, in glacial acetic acid, or in alcohol containing a little sulphuric or acetic acid, the sulphonic group is eliminated and a blue or green *sulphate* is obtained, from which ammonia liberates a red or brown *base*. The latter substance may be a *hydrazone*,



or it may have been produced by the condensation of two molecules of the hydrazine with one of the aldehyde $(C_{14}H_{15}N_4)_2CH \cdot C_6H_4X$, as in the case of salicylaldehyde already described. The investigation of these substances is difficult; both of them may be formed at the same time, and the conditions favouring the formation of each have not yet been ascertained. Benzaldehyde and salicylaldehyde, ($X = H, OH$), form both a *hydrazone*, melting in the former case at $159-160^\circ$, and a trimolecular condensation *product*, melting in the latter case at 130° ; *m*- and *p*-nitrobenzaldehydes, ($X = NO_2$) form only *hydrazones*, which melt at 177° and $160-161^\circ$ respectively; and cinnamaldehyde, forms only a trimolecular condensation *product* melting at 124° . *m*-Bromobenzaldehyde yields a *base* melting at 137° of which the constitution has not yet been elucidated. C. F. B.

Probable Constitutional Formula of the Sulphonic Acid, $C_{12}H_{12}O_3N_4S$, formed by the Action of SO_2 on a Diazobenzene Salt. JULIUS TRÖGER, H. BERLIN, and M. FRANKE (*Arch. Pharm.*, 1906, 244, 326—335. Compare this vol., i, 120, and the preceding abstracts).—The acid has the character of a hydrazine derivative, $C_6H_5 \cdot N:N \cdot C_6H_4 \cdot NH \cdot NH \cdot SO_3H$. Ammoniacal silver and copper solutions convert it respectively into the *silver* and *ammonium* salts of an acid containing two atoms of hydrogen less in the molecule, $C_6H_5 \cdot N:N \cdot C_6H_4 \cdot N:N \cdot SO_3H$.

The first acid condenses, when suspended in glacial acetic acid and treated with aromatic aldehydes, $C_6H_4X \cdot CHO$, to yellow or red *hydrazones*, $C_6H_5 \cdot N:N \cdot C_6H_4 \cdot NH \cdot N:CH \cdot C_6H_4X$; these have the character of mono-acid bases, and unite with the sulphuric acid (produced by the elimination of the sulphonic group) to form a blue or green *sulphate*, which is decomposed more or less by hot water, completely by ammonia. No products were obtained that proceeded from the condensation of two molecules of the hydrazinesulphonic acid with one of the aldehyde. Hydrazones were obtained with benzaldehyde, *m*- and *p*-nitrobenzaldehydes, salicylaldehyde, anisaldehyde,

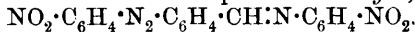


and cinnamaldehyde; they melt at $168.5-169^\circ$, $198-199^\circ$, 173° , 206° , 132° , and 167° respectively. C. F. B.

Condensation of the Three Nitroanilines with *p*-Nitrosobenzaldehyde. FREDERICK J. ALWAY and ROSS A. GORTNER (*Amer. Chem. J.*, 1906, 36, 510—515).—The ease with which the nitroanilines condense with *p*-nitrosobenzaldehyde varies with their basicity; thus, *m*-nitro-

aniline condenses readily, *p*-nitroaniline less readily, and *o*-nitroaniline so feebly that the condensation product could not be isolated.

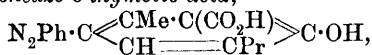
The *m*-nitroanil of *m*-nitrobenzene-*p*-azobenzaldehyde,



obtained by the condensation of *m*-nitroaniline with *m*-nitrosobenzaldehyde, forms brick-red, granular masses, melts at 239.5° (corr.), is readily soluble in nitrobenzene and sparingly so in alcohol or glacial acetic acid, and by prolonged treatment with hot, dilute hydrochloric acid is resolved into *m*-nitrobenzene-*p*-azobenzaldehyde and *m*-nitroaniline. *m*-Nitrobenzene-*p*-azobenzaldehyde crystallises in minute, red needles, melts at 135° (corr.) and is very soluble in alcohol, glacial acetic acid, or nitrobenzene; the substance previously described under this name (Abstr., 1904, i, 953) contained a large proportion of the *m*-nitroanil. The phenylhydrazone of *m*-nitrobenzene-*p*-azobenzaldehyde crystallises in dark red, rectangular plates and melts at 213.5° (corr.). The oxime separates from dilute alcohol in yellow crystals and melts at 116° (corr.). The anil forms small yellow crystals, and melts at 132° (corr.).

The *p*-nitroanil of *p*-nitrobenzene-*p*-azobenzaldehyde crystallises in small red needles, melts at 237–238.5° (corr.), and is sparingly soluble in alcohol but readily so in hot acetic acid. *p*-Nitrobenzene-*p*-azobenzaldehyde crystallises in long, red plates, melts at 221–222° (corr.), and is very soluble in hot benzene, glacial acetic acid, nitrobenzene, or amyl alcohol. The anil forms stellate groups of orange-coloured needles, melts at 152° (corr.), and is insoluble in alcohol. The oxime is a yellow solid which does not melt below 290°. E. G.

Reduction of Azo-derivatives of Aromatic Hydroxy-acids by Phenylhydrazine. ERNESTO PUXEDDU (*Gazzetta*, 1906, 36, ii, 305–313).—*Benzeneazo-o*-thymotic acid,



prepared by the action of diazobenzene sulphate on *o*-thymotic acid dissolved in sodium hydroxide solution, crystallises from alcohol or benzene in orange-yellow, prismatic needles melting at 185–195°, and dissolves in the more common organic solvents. It gives an intensely reddish-brown coloration with ferric chloride, dissolves in concentrated sulphuric acid to a cherry-red, in concentrated hydrochloric acid to a straw-yellow liquid, and in alkali solutions to a blood-red liquid. When it is reduced by means of phenylhydrazine, the N₂Ph group is doubtless replaced by NH₂, but the compound thus formed loses carbon dioxide, giving the corresponding aminothymol melting at 178°.

The reduction of benzeneazo-*m*-hydroxybenzoic acid by means of phenylhydrazine proceeds with explosive violence, and yields 6-amino-3-hydroxybenzoic acid.

o-Tolueneazo-*m*-hydroxybenzoic acid, C₁₄H₁₂O₃N₂, crystallises from alcohol in yellow, prismatic needles melting at 240°, and dissolves readily in the more common organic solvents. It is completely insoluble in dilute acids, but dissolves in concentrated acids, giving, with nitric acid, a deep red colour, disappearing on heating, and with sulphuric acid an intense blackish-brown liquid. Reduction with phenylhydrazine yields 6-amino-3-hydroxybenzoic acid.

p-Tolueneazo-m-hydroxybenzoic acid, $C_{14}H_{12}O_3N_2$, crystallises from alcohol or a mixture of alcohol and benzene in shining, prismatic needles, and melts and decomposes at 233° . It dissolves in organic solvents, in dilute alkali solutions, and in concentrated acids, being reprecipitated from the last-named by addition of water. Its reduction by means of phenylhydrazine proceeds explosively, and yields 6-amino-3-hydroxybenzoic acid.

m-Chlorobenzeneazo-m-hydroxybenzoic acid, $C_{13}H_9O_3N_2Cl$, crystallises from alcohol in orange-red, prismatic needles melting at $225-227^\circ$, and is soluble in concentrated acids, dilute alkali solutions, or organic solvents. Its reduction with phenylhydrazine takes place with explosive violence and yields 6-amino-3-hydroxybenzoic acid.

p-Chlorobenzeneazo-m-hydroxybenzoic acid crystallises from alcohol in orange-yellow, prismatic needles melting and decomposing at $235-236^\circ$ and is soluble in organic solvents, concentrated acids, or dilute alkali solutions. When reduced with phenylhydrazine, it gives 6-amino-3-hydroxybenzoic acid.

T. H. P.

The Oxidation of Benzidine. RICHARD WILLSTÄTTER and LUDWIG KALB (*Ber.*, 1906, **39**, 3474—3482).—This investigation was undertaken with the object of ascertaining the nature of a yellow, crystalline oxidation product of benzidine, obtained by oxidising the diamine with silver oxide or lead peroxide in inert solvents. This object has been attained by preparing the substance synthetically from 4-nitro-4'-aminodiphenyl, the *acetyl* derivative of which crystallises in prisms and melts at 240° .

4 : 4'-Diamino-4' : 4'-azodiphenyl, $N_2(C_6H_4 \cdot C_6H_4 \cdot NH_2)_2$, obtained by reducing 4-nitro-4'-aminodiphenyl with zinc dust and alcoholic sodium hydroxide, corresponds in every respect with the product of the oxidation of benzidine (*Abstr.*, 1905, i, 361); it crystallises in microscopic, yellowish-red needles, melts at 287° , and develops a characteristic blood-red coloration with concentrated sulphuric acid. The salts of this base with the mineral acids are insoluble in water; the *mono-hydrochloride*, $C_{24}H_{20}N_4 \cdot HCl$, consists of small, brown prisms; the *dihydrochloride*, $C_{24}H_{20}N_4 \cdot 2HCl$, is amorphous.

s-Diacetyl-4 : 4'-diamino-4' : 4'-azodiphenyl, produced from the diamine by the action of acetic anhydride, melts indefinitely and decomposes at 373° .

Tetra-azo-azodiphenyl chloride, $N_2(C_6H_4 \cdot C_6H_4 \cdot N_2Cl)_2 \cdot 2H_2O$, is produced most readily by diazotising the corresponding diamine with a large excess of hydrochloric acid (1 per cent.) and aqueous sodium nitrite (10 per cent.), when the salt is precipitated from the clear solution thus obtained by the addition of concentrated hydrochloric acid. The chloride, which consists of prismatic crystals having a violet reflex, gives an orange-red streak; it is moderately stable in air, and decomposes violently at about 95° . The tetra-azo sulphate and nitrate are both crystalline, the latter being exceptionally insoluble; the *platinichloride*, $C_{24}H_{16}N_6PtCl_6 \cdot H_2O$, is an insoluble, yellow, flocculent precipitate.

G. T. M.

Action of Diazo-compounds on α -Hydroxynaphthoic Acids. EUGÈNE GRANDMOUGIN (*Ber.*, 1906, **39**, 3609—3611. Compare Nietzki and Guitermann, *Abstr.*, 1887, 732; Reverdin and De la Harpe, *Abstr.*, 1893, i, 478).—The action of diazobenzene chloride on 1-hydroxy-2-naphthoic acid in alkaline solution, leads to the formation of dibenzeneazo- α -naphthol (Noelting and Grandmougin, *Abstr.*, 1891, 1076), which is formed also by the action of diazobenzene chloride on benzeneazo-1-hydroxy-2-naphthoic acid.

The reduction of benzeneazo-1-hydroxy-2-naphthoic acid by means of sodium hyposulphite in aqueous alcoholic solution (compare this vol., i, 716) leads to the formation of aniline and 4-amino-1-hydroxy-2-naphthoic acid (Nietzki and Guitermann, *loc. cit.*), which crystallises in slender, colourless needles, forms a crystalline *hydrochloride*, and yields 4-amino- α -naphthol when heated in a current of hydrogen chloride, or naphthaquinone when treated with nitrous acid. Aniline and 3 : 4-diamino- α -naphthol are obtained by reduction of dibenzeneazo- α -naphthol by means of sodium hyposulphite. G. Y.

Quinoneazines. By RICHARD WILLSTÄTTER and MAX BENZ (*Ber.*, 1906, **39**, 3482—3491).—4 : 4'-Dihydroxydiphenyl and 4 : 4'-dihydroxystilbene resemble catechol in being oxidised to quinonoid substances by silver oxide or lead peroxide, but 4 : 4'-dihydroxydiphenylmethane does not exhibit this behaviour. Hence it appears that the ethylene linking $\cdot\text{CH}\cdot\text{CH}\cdot$ does not sever completely the quinonoid relationship between the two benzene nuclei, whereas this connexion is quite annulled by the interposition of the methylene group. It is now shown that the azo-group is analogous to the ethylene group, the *p*-azophenols undergoing the characteristic oxidation.

p-Benzoquinoneazine, $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{O}$, prepared by shaking an ethereal solution of *p*-azophenol with silver oxide and fused sodium sulphate, crystallises from organic solvents either in dark orange-red prisms or needles or in dark yellow, rhombohedral leaflets or plates; both modifications have a blue reflex. When treated in dry ethereal solution with concentrated sulphuric acid the quinoneazine yields *p*-azophenol and an easily decomposable base; sulphurous acid or preferably phenylhydrazine reduces the quinoneazine to an azophenol which is not identical with ordinary *p*-azophenol.

The *quinkhydrone*, $\text{C}_{24}\text{H}_{18}\text{O}_4\text{N}_4$, of *p*-benzoquinoneazine separates in bluish-black needles with a bronze reflex on mixing ethereal solutions of *p*-azophenol and the quinoneazine; it melts at 181—182° and undergoes dissociation in alcoholic solution.

4 : 4'-Dihydroxystilbene when oxidised with lead peroxide or potassium ferricyanide gives rise to stilbenequinone, which is again reduced by phenylhydrazine to the original dihydroxy-compound.

p-Acetylaminodiazoaminobenzene, $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$, the intermediate product of the interaction of diazoacetanilide and aniline, crystallises in orange-yellow, acicular prisms and melts and decomposes at 150—152°.

p-Aminodiazoaminobenzene, $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, obtained by hydrolysing the foregoing compound with sodium ethoxide, crystallises

from dilute alcohol in brownish-yellow needles decomposing at 157° . Azoaniline, which is produced together with a preponderating amount of aminoazobenzene by warming the foregoing diazoamine with aniline and aniline hydrochloride, does not undergo the quinonoid oxidation on treatment with silver oxide or lead peroxide. G. T. M.

Ash-free Egg Albumin. R. W. ROSENKRANTZ (*J. Russ. Phys. Chem. Soc.*, 1906, 38, i, 2—3).—Crystals of egg-albumin obtained by a modification of the Hofmeister-Krieger process, are crystallised 6 to 10 times. They are then dissolved, dialysed, evaporated in a vacuum and again dialysed. Preparations so obtained give no ash on ignition, and do not contain recognisable quantities of ammonium sulphate. Z. K.

Complexes of Pure Albumin. ANDRÉ MAYER (*Compt. rend.*, 1906, 143, 515—516).—Pure ovalbumin, obtained from white of egg by diluting with water, filtering the precipitated globulins, recovering the albumin by prolonged dialysis, and repeating the processes several times, has a specific electrolytic conductivity of $1 \cdot 10^{-5}$, is not coagulated by heat, but forms soluble complexes with acids, (HCl , HNO_3 , H_2SO_4), bases (NaOH , KOH), or salts [NaCl , KCl , MgCl_2 , CaCl_2 , $(\text{NH}_4)_2\text{SO}_4$, MgSO_4 , Na_2SO_4 , K_2SO_4]. The amount of electrolyte absorbed by a definite quantity of ovalbumin, to raise the electrolytic conductivity from $1 \cdot 10^{-5}$ to $1 \cdot 10^{-4}$ varies with the nature of the electrolyte, being greater in the case of the acids than the bases or univalent salts, and greater in the case of the univalent than the bivalent salts. Ovalbumin forms insoluble complexes with salts of the heavy metals or positive colloids, which are soluble in dilute solutions of electrolytes and for this purpose $N/160$, HCl ; $N/140$, NaOH ; or $N/30$, NaCl are equivalent; from the solution a precipitate is formed by dilution or by dialysis, and the solution is coagulated by heating, the temperature at which coagulation occurs varying with the nature of the electrolyte used as the solvent. Thus a solution of an albumin-zinc salt coagulated at 56° , 60° , or 86° , according as it had been dissolved in hydrochloric acid, sodium chloride, or potassium hydroxide respectively. In respect of all these properties, the insoluble albumin complexes closely resemble the globulins, which may be regarded as complexes of pure albumin. M. A. W.

Distinction between Serum-albumin and Myo-albumin. JOSEPH DE REY-PAILHADE (*Bull. Soc. chim.*, 1906, [iii], 35, 1030—1031. Compare Abstr., 1904, i, 837; 1905, i, 728).—Aqueous extracts of the muscle of the cow, calf, horse, or turkey, and of whiting, evolve hydrogen sulphide on addition of sulphur, and this property is also exhibited by the coagulated albumins obtained by heating these extracts. The insoluble white residue, left after repeatedly washing horse-muscle with water, is almost inactive towards sulphur, and appears to behave as an inactive reserve for the more active and soluble myo-albumin. The latter is rendered inactive by contact with sulphur for several days, and the coagulum obtained from this is similarly inactive towards sulphur. An analogous non-philothionic myo-albumin may be obtained by extracting the uterus of

the sheep with dilute alcohol; the fresh tissue furnishes traces of hydrogen sulphide with sulphur, but the coagulum obtained by heating the alcoholic extract gives none.

T. A. H.

Philothionic Hydrogen. JOSEPH DE REY-PAILHADE (*Bull. Soc. chim.*, 1906, [iii], 35, 1031—1033. Compare preceding abstract and Heffter and Hausmann, *Abstr.*, 1904, i, 461).—The philothionic hydrogen of myo-albumin is not destroyed after 15 days' exposure to air at the atmospheric temperature, whereas it is much more rapidly removed by sulphur (see preceding abstract). In this connexion it is pointed out that hydrogen and sulphur combine at 250°, whereas hydrogen and oxygen do not unite below 350°, and it is suggested that whilst philothion seems to be capable of effecting the same chemical change as is induced by an increase in temperature of about 250°, its activity is insufficient to cause a combination which requires an increase of 350°.

T. A. H.

Monoamino-acids of the Crystalline Proteid from Pumpkin Seeds. EMIL ABDERHALDEN and OSCAR BERGHAUSEN (*Zeit. physiol. Chem.*, 1906, 49, 15—20).—The substances obtained from the cleavage of edestin (vitellin) by means of dilute sulphuric acid were: glycine, 0.08; alanine, present; aminovaleric acid, 0.7; leucine, 4.7; proline, 1.7; glutamic acid, 13.4; aspartic acid, 4.5; phenylalanine, 2.6; and tyrosine, 1.4 per cent.

W. D. H.

Optical Rotation of Gliadin in Certain Organic Solvents. W. E. MATHEWSON (*J. Amer. Chem. Soc.*, 1906, 28, 1482—1485. Compare this vol., i, 545).—The specific rotatory powers of solutions of gliadin in methyl, ethyl, propyl, and benzyl alcohols, phenol, *p*-cresol, and glacial acetic acid have been determined, and the results are tabulated. The gliadin was prepared from wheat-flour, and the experiments were made in connexion with an investigation which is in progress with a view to the improvement of the methods of flour analysis.

E. G.

Iodospongins. Preliminary Note. L. SCOTT (*Chem. Centr.*, 1906, ii, 1133; from *Biochem. Zeit.*, 1906, 1, 367).—The non-digestible residue of sponge substance can be rendered soluble by treatment with concentrated sulphuric acid. The product is then digested with pancreatic juice until it no longer gives the biuret reaction. After separating the diamino-acids, an organic compound, rich in iodine, is obtained, which is purified from monoamino-acids by the fractional crystallisation of its copper salt.

P. H.

The Rendering Insoluble of Gelatin by Formaldehyde. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1906, [iii], 35, 872—879. Compare this vol., i, 614, 915).—When gelatin is soaked in a solution of formaldehyde, the insoluble product formed contains from 4 to 4.8 per cent. of the aldehyde. The rapidity with which the formaldehyde is absorbed under these conditions increases with the concentration of the solution, but is not

sensibly influenced by increase of temperature. Gaseous formaldehyde is absorbed more slowly by gelatin, but the product ultimately formed is similar to that obtained in the first case. The precipitate produced by mixing solutions of gelatin and formaldehyde contains unaltered gelatin.

Gelatin rendered insoluble by formaldehyde is slowly decomposed by hot water, and the formaldehyde may be completely eliminated by this means. The same decomposition is brought about by macerating the product in cold, dilute hydrochloric acid, and this method was used for the liberation and ultimate estimation of the formaldehyde by Seyewetz and Gibello's process (*Abstr.*, 1904, ii, 521). The formaldehyde is also gradually liberated from the insoluble product when the latter is heated at 110°. From these results it is concluded that when gelatin is treated with formaldehyde, an additive product rather than a true compound is formed.

T. A. H.

Intramolecular Absorption of Water in the Tryptic Digestion of Proteid. PAUL HÁRI (*Pflüger's Archiv*, 1906, 115, 52—63).—Elementary analysis shows that the products (peptone) of the action of trypsin on proteids contain more oxygen and more hydrogen than the original material. This is attributed to the intramolecular absorption of water.

W. D. H.

Tryptophan. CARL NEUBERG (*Chem. Centr.*, 1906, ii, 892; from *Charité Ann.*, 30).—The author suggests the following modification of Hopkins and Cole's method of preparing tryptophan. In the second precipitation with mercuric sulphate the first portions, consisting almost entirely of cystine and mercury-cysteine, should be rejected; the filtrate is then treated with hydrogen sulphide, and after boiling off the excess of the latter, an excess of lead carbonate is added (100 grams of lead carbonate per kilogram of casein). The whole is then warmed on a water-bath for half an hour, ammonia is added until the solution smells faintly, and the heating is continued for a quarter of an hour more. The dissolved lead is then precipitated by means of hydrogen sulphide and the solution is evaporated; perfectly pure, white tryptophan separates out in a yield of 7—8 grams per kilogram of well-digested casein.

P. H.

Myelin Bodies. J. G. ADAMI and L. ASCHOFF (*Proc. Roy. Soc.*, 1906, 78 B, 359—368).—The term myelin was originally applied by Virchow to a constituent of the white substance of nerves which swells up with water, and develops curious forms with a double contour. Myelin bodies have since then been described in many situations in cell protoplasm under both physiological and pathological conditions. Many soaps exhibit the same phenomena. The globules formed are doubly refracting, and the hypothesis is advanced that they are fluid sphærocrystals. With regard to their chemical composition there is still much doubt, but the evidence appears to point to two principal varieties, namely, cholesterol oleate and choline oleate.

W. D. H.

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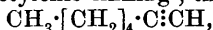
THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Molecular Refraction and Dispersion of Acetylenic Compounds. CHARLES MOUREU (*Compt. rend.*, 1905, 141, 892—895).—The author has measured the molecular refraction and dispersion of 30 acetylenic compounds (compare Abstr., 1902, i, 253, 289; 1903, i, 312, 698; 1904, i, 285, 286, 650, 811), and in the original the differences between the observed values and those calculated from the sum of the atomic refractions are recorded. If M represents the observed molecular refraction for the D line of sodium and C represents the corresponding calculated value, then the effect of the acetylenic linking, measured by $M - C$, is found to be constant for members of a homologous series, but to vary with different types of compounds, increasing with the number of negative groups in the molecule and their proximity to the acetylenic linking; thus, for heptinene,



and octinene, $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{C} \equiv \text{CH}$, $M - C$ has the minimum values 2·338 and 2·301 respectively, whilst the corresponding value for diphenyldiacetylene, $\text{CPh} \cdot \text{C} \equiv \text{C} \cdot \text{CPh}$, is 17·494 (compare Brühl, Abstr., 1894, ii, 432; Haller and Muller, Abstr., 1899, i, 770; ii, 622; 1904, ii, 221; Muller, Abstr., 1902, i, 354; Muller and Bauer, Abstr., 1904, ii, 705).

M. A. W.

Luminescence of Radium Bromide. B. WALTER and R. POHL (*Ann. Physik*, 1905, [iv], 18, 406—409. Compare Sir William and Lady Huggins, *Abstr.*, 1904, ii, 4).—The air in the neighbourhood of radium bromide is found to glow even at a distance of several centimetres from the salt. J. C. P.

The Doughty Springs : a Group of Radium-bearing Springs in Colorado. WILLIAM P. HEADDEN (*Proc. Colorado Sci. Soc.*, 1905, 8, 1—30 ; six plates).—At the base of a cliff of sandstone and shale on the North Fork of the Gunnison River, in Delta Co., Colorado, are a number of small springs of an exceptional type. The waters smell of hydrogen sulphide, and carbon dioxide is also liberated. Analyses of the waters of different springs show considerable variations in composition : sodium, calcium, barium, strontium, &c., chlorine, sulphuric, dithionic acids, &c., are present. The deposits of the different springs also vary widely in character. Of one, it consists mainly of ferrous sulphide with some manganous sulphide and zinc sulphide ; that of another spring is almost pure sulphur. On the cliffs there are efflorescences of gypsum, alums, alunogen, and mirabilite. The most abundant deposit is an extensive bed of sinter which, near the springs, consists of almost pure barium sulphate, whilst farther away it consists mainly of calcium carbonate with small amounts of barium sulphate. The baritic sinter is radioactive, and from it was obtained a barium chloride preparation which acts strongly on a photographic plate. L. J. S.

Chemical Separation of Radioactive Types of Matter in Thorium Compounds. HERMAN SCHLUNDT and RICHARD B. MOORE (*J. Physical Chem.*, 1905, 9, 682—706).—The successive changes in thorium compounds may be classified as thorium → thorium X → emanation → matters causing excited activity → final product, whilst the matters causing excited activity have been further divided into thorium A and thorium B, of which the latter alone emits rays (Slater, *Abstr.*, 1905, ii, 368). The thorium X is usually separated from thorium by precipitating the thorium as hydroxide by means of ammonia. The author shows that the thorium may be also precipitated as hydroxide by pyridine or as fumarate by fumaric acid. In each case the thorium X remains in the filtrate. The activity of the residue from the filtrate is greater than when ammonia is used for the separation, the precipitate being in a corresponding manner less active, and it is shown that this is due to thorium A, which remains in solution with the thorium X, but which is precipitated when ammonia is employed (compare *Abstr.*, 1905, ii, 789). L. M. J.

Radiation of Quinine Sulphate. ALFRED KALÄHNE (*Ann. Physik*, 1905, [iv], 18, 450—472).—The author confirms and supplements the results obtained by Le Bon (*Compt. rend.*, 1900, 130, 891), who showed that quinine sulphate, when heated suddenly to temperatures above 100°, exhibits a faint luminescence lasting for a short time. On cooling, the substance again becomes luminous for a short time. The radiation during the cooling of the quinine sulphate

imparts conductivity to the surrounding air and has the power of penetrating thin aluminium foil and glass. The cause of the radiation is the removal of water on heating and the absorption of water on cooling. When the heated and dehydrated sulphate is allowed to cool, water vapour being rigidly excluded, neither luminescence nor ionisation of the surrounding air is observed.

J. C. P.

Accumulators of Material other than Lead. KARL ELBS (*Zeit. Elektrochem.*, 1905, 11, 734—735).—In the Edison-Jungner accumulator, iron filings previously heated to redness, reduced by hydrogen, and then cathodically polarised, are used. In a concentrated solution of potassium hydroxide, such iron acts as a moderately good anodic depolariser; it appears to be oxidised to ferrous hydroxide, but the oxidation never penetrates much below the surface. Hydrogen is evolved even at the beginning of the charging period. The positive plate consists of a mixture of nickel hydroxide and graphite; the substance formed in charging is always the nickelic hydroxide, Ni(OH)_3 , which is reduced to nickelous hydroxide, Ni(OH)_2 , during discharge. The action of the accumulator may therefore be represented by the equation $\text{Fe} + 2\text{Ni(OH)}_3 \rightleftharpoons \text{Fe(OH)}_2 + 2\text{Ni(OH)}_2$. The *E.M.F.* of the cell is 1.42—1.48 volts, which sinks on discharge to 1.35—1.37 volts.

T. E.

Accumulators of Material other than Lead. GRÄFENBERG (*Zeit. Elektrochem.*, 1905, 11, 736—739).—Some details of the manufacture of the Jungner accumulator are given. A cell weighing 3 kilograms gives about 50 watt hours under normal conditions, the volume of the cell is 1.45 litres. In charging, the *E.M.F.* required rises to nearly 1.8 volts, whilst in discharging it falls to 1.23 volts. A large quantity of oxygen and hydrogen is evolved during the charge. On standing, the cells lose as much as 10 per cent. of their charge in twenty-four hours. In practice, the energy efficiency is scarcely more than 40 per cent.

T. E.

The Specific Inductive Capacity of Water and Benzene. F. BEAULARD (*Compt. rend.*, 1905, 141, 656—658).—The author discusses the theories of dielectrics of Poisson and Mossotti and of Faraday. The liquids examined were enclosed in a thin glass ellipsoid and placed in a Hertzian field, obtaining for benzene (containing traces of thiophen) a mean value of $K=1.657$, and for very pure water 11.04, a number much less than that generally assumed. By substituting a quartz vessel for the glass ellipsoid, it may be possible to avoid the effects of hysteresis.

F. G. C. S.

Relation between Electrolytic Conduction, Specific Inductive Capacity, and Chemical Activity of Certain Liquids (with a Bibliography of Dielectric Constants). JOSEPH HOWARD MATHEWS (*J. Physical Chem.*, 1905, 9, 641—681).—Numerous exceptions to the Nernst-Thomson rule have been recorded by various observers (Schlundt, *Abstr.*, 1901, ii, 299; Kahlenberg, *Abstr.*, 1904,

ii, 225), and the author has therefore determined the conductivity and dielectric constant of a very large number of solutions in various solvents, and made many redeterminations of the values obtained by Eggers (Abstr., 1904, ii, 224), Walden (Abstr., 1903, ii, 408), and others. A large number of solutions in allylthiocarbimide and other thiocarbimides was examined. A few of the acids, and iodine, form conducting solutions; otherwise the solutions in general do not conduct. An attempt was made to prepare and examine thiocyanic acid, but, owing to its extreme instability and rapid polymerisation, even at low temperatures, no conductivity experiments could be made. The unpolymerised acid, however, showed complete absorption, and the dielectric constant of the polymeride was 4.9. In methyl and ethyl silicates, the solution of trichloroacetic acid does not conduct, but it is readily acted on by metallic magnesium. A number of similar cases are also recorded. Thus, the solution of trichloroacetic acid in nitrobenzene (which has a high dielectric constant, 34.0), is readily acted on by zinc, magnesium, or sodium, and similar results were obtained with other acids. The idea that minute traces of water cause many abnormal results in conductivity experiments is shown to be erroneous, as an amount greatly in excess of that present in the ordinary dried sample of a solvent is required before conductivity is given to a non-conducting solution.

A very complete bibliography of work relating to dielectric constants is added to the paper. L. M. J.

Molecular Conductivity of Phosphoric Esters. PAUL CARRÉ (*Compt. rend.*, 1905, 141, 764—766).—The molecular conductivities at 25° of the *mono*-phosphoric esters of the type $\text{OR} \cdot \text{PO}(\text{OH})_2$ (compare Abstr., 1905, i, 814) have been determined by Kohlrausch's method, and the results are given in the following table:

Molecular conductivity μ .

Phosphoric acid.	Di-hydrogen ethyl phosphate.	Di-hydrogen isobutyl phosphate.	Di-hydrogen glyceryl phosphate.	Di-hydrogen glyceryl phosphate.	Di-hydrogen erythran phosphate.	Di-hydrogen mannide phosphate.	Dilution, 1 gram-mol. in
96	156	152	193	190	212	208	8 l.
124	192	189	228	226	252	242	16
156	241	237	265	263	283	274	32
195	279	275	297	294	311	302	64
240	312	308	326	322	338	329	128
279	341	337	342	339	356	347	256
317	369	366	358	354	370	364	512

from which it will be seen that the mono-esters have a higher molecular conductivity than the free acid, the value depending on the number of carbon atoms in *R* and on its nature; thus, when *R* represents homologous groups, the lower member of the series has the higher value.

The di-esters of phosphoric acid, $\text{OH} \cdot \text{PO}(\text{OR})_2$, are not sufficiently stable in aqueous solution to admit of conductivity determinations, but a mixture of dihydrogen erythranphosphate, $\text{PO}(\text{OH})_2 \cdot \text{O} \cdot \text{C}_4\text{H}_7\text{O}_2$, with 37 per cent. of the di-ester, $\text{OH} \cdot \text{PO} \left\langle \begin{array}{c} \text{O} \cdot \text{CH} \cdot \text{CH}_2 \\ \text{O} \cdot \text{CH} \cdot \text{CH}_2 \end{array} \right\rangle \text{O}$, gave

$\mu = 232$ for a dilution of 1 gram-mol. in 8 litres, the corresponding value for the mono-ester being 212; it is probable, therefore, that the di-esters of phosphoric acid have a higher molecular conductivity than the mono-esters.

M. A. W.

Numerical Values of Electrode Potentials. ROBERT LUTHER (*Zeit. Elektrochem.*, 1905, 11, 777—780).—If the potentials of two electrodes, *B.b* and *C.c*, have been measured against the same electrode, *A.a* (the capital letters refer to the electrodes, the small letters to the electrolytes), it is possible to calculate the *E.M.F.* of the cell *B.b.a.c.C* exactly, and that of the cell *B.b.c.C* approximately, by neglecting the small potential difference between the electrolytes *b* and *c*. On the whole, the calomel electrode is preferable to the hydrogen electrode as the standard of comparison, because with potassium chloride the diffusion *E.M.F.* between the electrolytes can be calculated with less inaccuracy than in any other case; it is also more exactly reproducible than the hydrogen electrode. The numerical value of an electrode potential depends on the value used for the standard electrode; this value is purely a matter of convenience; the three values in use for the calomel electrode (0.560 volt, 0.283 volt, and zero) are all based on more or less hypothetical grounds.

The author also proposes to use the positive sign for all electrodes which are positive to the standard electrode adopted.

T. E.

Numerical Values of Electrode Potentials. FRIEDERICH KRÜGER (*Zeit. Elektrochem.*, 1905, 11, 780—784).—The importance of the potential differences between electrolytes is insisted on; they may exceed 0.1 volt in extreme cases. It is better to make them small by using the calomel electrode for neutral solutions and the hydrogen electrode for acid solutions. The two electrodes are equally accurate, although the calomel electrode has the advantage of being independent of the atmospheric pressure.

The great convenience of using the potential of the normal hydrogen electrode as the zero point of the scale of potentials is that the metals are thus divided into two groups, the potentials of those which are precipitated by hydrogen of atmospheric pressure lying on one side of zero and the potentials of those which set hydrogen at liberty from a normal solution of hydrogen ions on the other.

T. E.

Electrolysis with Alternating Current. MAX LE BLANC (*Zeit. Elektrochem.*, 1905, 11, 705—708).—The experiments previously described (*Abstr.*, 1904, ii, 229) have been extended. Supposing that an alternating current has no specific action different from that of a direct current, an unsymmetrical alternating current in which one impulse lasts three times as long as the succeeding one in the opposite direction should produce the same result as a direct current of half the strength. This was shown to be the case with copper electrodes in a 2*N* solution of copper sulphate with a current density of 0.046 ampere per sq. cm. Copper electrodes which have been heated in the flame of a blowpipe until fusion begins, and then quenched in alcohol, show a

smooth, even surface. When such electrodes are used under the conditions mentioned above, the one which is the cathode during the long current impulse gains more than the anode loses. The copper behaves as if its valency was less than two. This "noble" copper (in a normal solution of copper sulphate) gives a difference of potential of 13 millivolts against ordinary copper.

As a rule, the quantity of a metal which is dissolved by an alternating current diminishes regularly as the number of alternations per minute increases. Brochet and Petit have noticed, however, that in some cases the curve passes through a maximum. Nickel in 4*N* potassium cyanide solution gives such a maximum with a current density of 0.2 ampere per sq. cm., whilst with 0.07 ampere per sq. cm. it does not. With direct current of the higher density, nickel is passive, whilst with the lower value it dissolves quantitatively. The author therefore ascribes the increase of dissolution with increase of frequency of the current to a diminution of the passivity; the subsequent diminution of the quantity of dissolved metal with still higher frequencies is explained as before (Abstr., 1904, ii, 229).

T. E.

Oxidation of Nitrogen in the High Tension Flame. JOHANNES BRODE (*Zeit. Elektrochem.*, 1905, 11, 752—754).—In the flame produced by a high tension electric discharge in air, three zones can be distinguished. The introduction of a non-conductor into the two upper zones does not affect the current flowing; this is not so for the lowest zone which, therefore, is the path of the discharge and the hottest part of the flame. The temperature cannot be measured directly, but it is possible to get from the flame gases containing 8 per cent. of nitric oxide, which, according to Nernst's measurements, would indicate a temperature of at least 3700°. Gas drawn off through a cold platinum capillary tube from the uppermost zone of the flame contains more nitric oxide than gas taken from the space surrounding the flame, from which it appears that the decomposition of nitric oxide is the reaction occurring in the upper zone. The middle zone cannot be examined directly, since a cold object deflects it. The discharge in nitrogen or hydrogen, however, corresponds entirely with the lowest zone of the air flame. In oxygen, the two lower zones are present; it is probable, thus, that the middle zone of the air flame is due to the decomposition of ozone. The formation of ozone in the flame discharge in oxygen was shown by producing the discharge in a water-cooled quartz tube through which a current of pure oxygen passed. Oxygen flowing through a parallel quartz tube contained no ozone, showing that, in this case, ultra-violet light was not the cause of the formation of ozone.

T. E.

Glow Discharge in the Halogens, Chlorine, Bromine, and Iodine. W. MATTHIES (*Ann. Physik*, 1905, [iv], 18, 473—494. Compare Abstr., 1905, ii, 793).—The normal potential fall at a platinum cathode increases with the molecular weight of the halogen; the mean values are: in chlorine 295 volts, in bromine 335 volts, in iodine 377 volts. The differences between the potential falls in the

halogens and in the corresponding mercury haloids are nearly equal for the three cases. J. C. P.

The Specific Heat of Copper Sulphate Solutions. P. VAILLANT (*Compt. rend.*, 1905, 141, 658—660).—Joule's method was employed, using a Berthelot calorimeter, the spiral being replaced by an incandescent electric lamp. The method consists in finding the number of joules required to raise the liquid through a definite interval. This method gives negative values for the specific heat of the molecule CuSO_4 (as obtained by Thomsen and Marignac), but for the molecule $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ the specific heat at first increases rapidly with the concentration and then passes through a maximum.

This is explained by the increase of the molecular volume of the substance with its dilution and by electrolytic dissociation which sets free the water of hydration, and by the formation of a hydrate with less than $5\text{H}_2\text{O}$ in very concentrated solutions.

The calculated specific heat of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is 0.2832. F. G. C. S.

Kinetics of Extreme States of Aggregation. EMIL BOSE (*Zeit. Elektrochem.*, 1905, 11, 742—744).—The passage of heat between two plates separated by a very dilute gas is considered for the case that the distance between the plates is small compared with the mean free path of the gas molecules. An expression is also given for the friction between the gas and a solid.

Assuming that in dilute gases the gas molecules strike the vibrating molecules of the solid wall so that their average velocity is unchanged, the mean velocity of the molecules of the solid may be calculated. The period of vibration calculated from the index of refraction makes it possible then to calculate the amplitude of the solid molecules. The numerical results obtained show that the amplitude is always considerably less than the mean distance between the molecules, and that for different substances the amplitudes change in the same way as the coefficients of expansion. T. E.

Determination of the Critical Point of Hydrogen. KARL OLSZEWSKI (*Bull. Acad. Sci. Cracow*, 1905, 399—406. Compare Abstr., 1896, ii, 9; 1902, ii, 444).—An historical account of the determination of the critical point of hydrogen, and a claim for priority as against Wroblewski. G. Y.

Expansion of Hydrogen. AUGUST W. WITKOWSKI (*Bull. Acad. Sci. Cracow*, 1905, 305—338. Compare Wroblewski, Abstr., 1887, 563).—If the temperature of a gas is altered from 0° to θ° , the pressure remaining constant, the change in volume is expressed by the equation $v = \eta_0(1 + a_{p\theta}\theta)(p_0 v_0/p)$, in which η_0 is a function of the pressure and $a_{p\theta}$ of the pressure and the temperature θ . The author has determined the coefficient of expansion a for hydrogen, for temperatures between 100° and -212° , and for pressures not exceeding 60 atmospheres. Two glass vessels of volumes s_0 and s are filled with hydrogen under the pressure p ; the temperature of the one is main-

tained at 0° , whilst the other is heated or cooled to θ° . Thus, there are obtained the expressions $M_0 = ps_0/\eta_0$ and $M = ps/\eta_0(1 + \alpha_{p\theta}\theta)$, from which follow $\alpha_{p\theta} = M_0s/Ms_0\theta - 1/\theta$ and $\eta_\theta = \eta_0(1 + \alpha_{p\theta}\theta)$. The temperatures were determined by means of a hydrogen thermometer. As the compressibility of hydrogen does not follow Boyle's law exactly, the pressure, instead of $p' = M_0/s_0$, is $p = M_0\eta_0/s_0 = \eta_0p'$, with $p = p' + \Delta$. The value of Δ at 0° varies from 0.001 for a pressure of 2 atmospheres to 2.331 for 60 atmospheres, whilst that of η_0 varies from 1.0000 at 1 atmosphere to 1.0373 at 60 atmospheres pressure.

The results of the determinations of the coefficient of expansion α are plotted as isobars with the values of α as ordinates and the temperatures as abscissæ, and as isothermal lines with the pressures as abscissæ. For a pressure of 60 atmospheres at -212° , $\alpha = 0.00384$, diminishing to 0.00368 at -150° and 0.003557 at 100° ; as the pressure diminishes, the isobars are flattened, that for 10 atmospheres approaching a straight line, with $\alpha = 0.00371$ at -212° , 0.003668 at -150° , and 0.003645 at 100° .

The isothermals radiate in straight lines from a point at about $\alpha = 0.00367$ under 1 atmosphere pressure to $\alpha = 0.003841$ for -212° , and 0.003558 for 100° under 60 atmospheres pressure.

The value of η_θ in the equation $\eta_\theta = \eta_0(1 + \alpha_{p\theta}\theta)$ is calculated from the coefficient of expansion, and found to rise with the temperature and, above -183° , with the pressure, the maximum value being 1.4064 at 100° under 60 atmospheres pressure. The compressibility curves drawn from the values of η at -183° , -190° , -205° , and -212° , have the minima 0.3270 under 32 atmospheres, 0.2970 under 43.5 atmospheres, 0.2273 under 55 atmospheres, and 0.1926 under 54.8 atmospheres pressure respectively (compare Wroblewski, *loc. cit.*).

Tables are given of the pressure of hydrogen at densities 5–60 and of the value of $\Delta = p_0[1 + (0.0036612 + 0.000000984/v)\theta] - p$ at temperatures 100° to -212° .

The author's results are expressed finally in the characteristic equation for hydrogen, $p_v = (0.999384 + 0.0006154/v + 0.000000706/v^2)[1 + (0.036612 + 0.000000984/v)\theta] - l(\theta) - m(\theta)/v$. G. Y.

Determination of Melting Points in Capillary Tubes. RUDOLF WEGSCHEIDER (*Chem. Zeit.*, 1905, 29, 1224–1225).—It is pointed out that the determination of melting points in capillary tubes hardly ever gives a sharp melting point, but rather a temperature interval within which the substance melts, inasmuch as the thermometer nearly always records a higher temperature at the moment that the substance has completely fused than it did when the substance began to melt; this is probably due to the fact that the substance at the centre of the tube is at a lower temperature than the surrounding portions; a second reason is probably to be found in the fact of the substance not being absolutely pure. In the case of substances which decompose at or below their melting points, it is desirable to raise the temperature as rapidly as possible or to introduce the substance into a melting-point bath heated previously, otherwise the melting point observed is, in reality, that of a mixture of the substance with its decomposition products. In all such cases it is desirable to

record the exact conditions under which the melting point was determined. P. H.

Boiling Points of Aqueous Solutions. S. M. JOHNSTON (*Proc. Roy. Soc. Edin.*, 1905, 25, 952—966).—The author has observed that in boiling point determinations, the boiling point of the solvent can be raised or lowered within the range of some hundredths of a degree by increasing or decreasing the strength of the source of heat, but that a solution in the same circumstances takes up a definite unvarying temperature. It is hence seen that determinations of molecular weight are obtained with greater accuracy by finding the boiling-point elevation by adding salt to a solution and not to the solvent. The experimental results show a far greater constancy for the elevation constant when this is done. L. M. J.

Vapour Pressure of some Solids. EILHARD WIEDEMANN, K. STELZNER, and G. NIEDERSCHULTE (*Verhandl. Deut. Phys. Ges.*, 1905, 7, 159—162).—The vapour pressure was determined over a wide range of temperature for mercuric chloride, bromide, and iodide, mercurous chloride and iodine. The values at low temperatures were determined by the loss of weight in an air current; at high temperatures, pressure and temperature were read during sublimation of the solid. Tables of the results are given; the author states that the values by the two methods agreed well, but does not indicate in the tables what values were obtained by both methods. It is seen that the vapour pressure of the mercury haloids decreases with increasing molecular weight, although the values for mercuric chloride and bromide are almost identical up to about 230°. L. M. J.

Vapour Pressure of Mercury and Sodium. A. GEBHARDT (*Verhandl. Deut. Phys. Ges.*, 1905, 8, 184—188).—The values obtained for the vapour pressure by the dynamical method are in close agreement with those obtained by Ramsay and Young and by Hertz.

The method was also used for sodium, a boiling vessel of porcelain being employed and temperatures being read by a platinum—platinum-rhodium thermoelement. The values obtained are :

380°	1.2 mm.	500°	8.6 mm.
410°	1.7 „	530°	15.0 „
440°	2.9 „	550°	23.0 „
470°	5.1 „	570°	80.0 „

These values are very different from those obtained by Jewett (*Abstr.*, 1903, ii, 61), who found the pressure at 420° to be 14.4 mm., and this the author ascribes to the use by Jewett of a glass vessel.

L. M. J.

Method of Determining the Osmotic Pressure of very Small Quantities of Liquid. HARTOG J. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 394—397).—When only 0.25—0.5 c.c. of a solution is available, the osmotic pressure may be determined by

a method based on the principle already known, that the volume of blood corpuscles is dependent on the osmotic pressure of the solution containing them. The solution to be examined is put in a small funnel-shaped glass tube, the cylindrical neck of which is formed by a calibrated capillary, closed below. Other similar tubes contain sodium chloride solutions of gradually increasing concentration. To each tube, 0.02 c.c. of blood is added. At intervals, the tubes are centrifuged until the volume of the sediment in each case no longer alters. The osmotic pressure of the solution under examination is the same as that of the sodium chloride solution, in which the sediment of blood corpuscles occupies the same volume.

By this method, the author found that the osmotic pressure of the lachrymal fluid is the same as that of a 1.4 per cent. sodium chloride solution. The method can be successfully applied also with blood serum, lymph, cerebrospinal fluid, and saliva. J. C. P.

Employment of Thermal Analysis. III. GUSTAV TAMMANN (*Zeit. anorg. Chem.*, 1905, 47, 289—313. Compare Abstr., 1904, ii, 113; 1905, ii, 444).—A theoretical paper. In two former papers, it was shown how the author's method of thermal analysis can be employed for determining the composition of chemical compounds occurring in alloys. In the present paper, further applications of the method are described, more particularly with regard to the composition of mixed crystals. G. S.

Applicability of van der Waals' Equation to the Solid State. CARL BENEDICKS (*Zeit. anorg. Chem.*, 1905, 47, 455—463. Compare Traube, Abstr., 1903, ii, 355).—A criticism of the proofs advanced by Traube (*loc. cit.*) to show that van der Waals' equation is applicable to the solid state.

Putting v as the atomic volume, $v-b$ as the co-volume, and β as the expansion coefficient of a solid substance, Traube has found that the expression $v.3\beta/v-b$, which may be regarded as the expansion coefficient of the co-volume, has the value $1/273$, and is therefore the same as for gases. The author shows that this is a direct mathematical consequence of employing van der Waals' equation, and does not prove that the relation in question actually holds. The same criticism applies to Traube's observation that the internal pressures calculated by him from the expression a/v^2 are proportional to those calculated by Richards (compare Abstr., 1902, ii, 304) on quite different assumptions; it happens that van der Waals' equation approximately fulfils a condition of Richards' theory, but it is by no means the only equation which does so.

On the other hand, Traube's observation that the expression a/v^2 , the "internal pressure," is proportional to hardness in the case of solid elements is confirmed and illustrated graphically.

The author does not deny that van der Waals' equation may hold for solids, but for the reasons given considers that strict proof of its applicability is still wanting. G. S.

Deduction of Several Common Formulæ from a General Equation of State. G. VAN ITERSON, jun. (*Zeit. physikal. Chem.*, 1905, 53, 633—640).—Starting only with the general equation $F(p, v, T, a, b, c) = 0$, in which F is a function independent of the nature of the substance, and a , b , and c are mutually independent constants for a given substance, and postulating that this general equation must for high values of v and T and low values of p assume the form $pv = RT/m$, where m is molecular weight and R is the absolute gas constant, the author deduces a number of well-known formulæ. Among these are $R/m \cdot \theta_0 / \pi_0 \phi_0 = C$; $\pi_{lv} = f_1(\theta)$, $\phi_l = f_2(\theta)$, and $\phi_v = f_3(\theta)$; in these equations, π_{lv} is the reduced pressure of saturated vapour, ϕ_l is the reduced volume of the liquid, ϕ_v is the reduced volume of the vapour, θ is reduced temperature, and f_1, f_2, f_3 are functions independent of the nature of the substance. Combination with the Clausius-Clapeyron formula leads to Guldberg's rule, according to which the boiling points of different substances under atmospheric pressure are approximately corresponding temperatures, and also to Trouton's rule. Combination with Mathias and Cailletet's law of the rectilinear diameter leads to another empirical rule given by Guldberg, namely, $v_0 = r \cdot \phi_0$, where v_0 is the volume at the absolute zero and r is an absolute constant (see *Abstr.*, 1900, ii, 264). J. C. P.

Equilibrium in the System : Bismuth and Sulphur. A. H. W. ATEN (*Zeit. anorg. Chem.*, 1905, 47, 386—398).—Largely theoretical. The conclusions drawn by Pelabon (compare *Abstr.*, 1904, ii, 42) from his experimental investigation of this system are criticised.

The freezing point curve of mixtures of bismuth and sulphur up to 52 atom. per cent. of the latter has been investigated and represented in the usual way by plotting solidification temperatures as ordinates against the atom. percentage composition in sulphur as abscissæ. The curve rises rapidly from the bismuth axis until the mixture contains about 10 atom. per cent. of sulphur; between 10 and 45 per cent. it is flatter, and from the latter point rises steeply as far as it can be followed. This agrees in the main with Pelabon's results, except that the latter found the curve flatter when equivalent proportions of the elements were present, from which he deduced the existence of a compound BiS . The author shows that even if Pelabon's observation is correct, it does not prove the existence of a compound of the above composition, since there is no maximum or transition point, and this conclusion is confirmed by determination of the cooling curve and by microscopic examination of mixtures containing the elements in varying proportions.

Pelabon regarded former results (*Abstr.*, 1901, ii, 165) obtained in studying the action of hydrogen on bismuth sulphide as confirming the existence of the compound BiS , because the composition of the gas phase at 440° up to 50 atom. per cent. of sulphur is independent of the proportion of the latter element present, but it is shown that this is in accordance with the phase rule, and it has not been proved that the composition of the gas does not remain constant with higher proportions of sulphur.

It is probable that up to 52 atom. per cent. of sulphur, mixtures of Bi_2S_3 and bismuth separate out.

The freezing-point curve of mixtures containing more than 52 atom. per cent. of sulphur cannot be determined, because the temperatures lie above the boiling point of this element. A theoretical discussion of such systems, in which the boiling-point curve of one of the constituents intersects the freezing-point curve, is given, and the results are represented graphically. G. S.

Reciprocal Salt Pairs. IV. A Problem of Affinity. WILHELM MEYERHOFFER (*Zeit. physikal. Chem.*, 1905, **53**, 513—603. Compare Abstr., 1896, ii, 414; 1899, ii, 410; 1900, ii, 198; 1901, ii, 639).—A detailed account of experiments made on the solubility and relative stability of the salt pairs $\text{BaCO}_3 + \text{K}_2\text{SO}_4$ and $\text{BaSO}_4 + \text{K}_2\text{CO}_3$. The results are discussed with the aid of the usual graphical representations, and do not lend themselves readily to abstraction. The knowledge gained by the use of the phase rule is supplemented by the application of the mass action law and the dissociation theory. Light is thus thrown on the process of fractional precipitation.

One or two points may be specially mentioned. It is shown that at the ordinary temperature $\text{BaCO}_3 + \text{K}_2\text{SO}_4$ is the stable system. The ratio $\text{K}_2\text{CO}_3:\text{K}_2\text{SO}_4$, which has hitherto been regarded as constant, is found to vary markedly with the potassium concentration and with the temperature. The system $\text{BaCO}_3 + \text{K}_2\text{SO}_4$ furnishes a case of incongruent melting, and barium sulphate separates when fusion takes place.

A method is described for the quantitative analysis of a mixture of the four solid salts. J. C. P.

Reaction Velocities at Low Temperatures. JOH. PLOTNIKOFF (*Zeit. physikal. Chem.*, 1905, **53**, 605—632).—Ethylene and bromine, when dissolved in light petroleum, combine with measurable rapidity at -78° . Ethylene bromide separates out, and the combination is accompanied by a contraction. If the reaction takes place in a vessel of the form of a dilatometer, the gradual contraction can be observed in the capillary tube, and the velocity of the reaction determined accordingly. The reaction between ethylene and bromine is in this way shown to be of the second order, and experiments made at various temperatures between -80° and -100° indicate that the temperature-coefficient for an interval of 10° has the very high value 6.2.

A large Dewar vacuum vessel was used as the thermostat in these experiments, and the temperature of -78° was obtained by using a mixture of alcohol and solid carbon dioxide. The lower temperatures were reached by the regulated addition of liquid air to the contents of the thermostat. The accurate determination of the reaction velocity from the change in volume of the reaction mixture was possible only after elimination of the volume changes due to slight temperature variations; this was effected by observing the fluctuations in volume of a liquid contained in a similar vessel and subject to the same external conditions. J. C. P.

Laws of the Action of Enzymes and Heterogeneous Catalysis. VICTOR HENRI (*Zeit. Elektrochem.*, 1905, 11, 790—793).—The velocity with which a substance is changed by an enzyme is sometimes proportional to the concentration of the unchanged substance in the solution, in other cases this is not true. The initial velocity may always be expressed by the formula $v = K.a/[1 + ma]$, in which K and m are constants and a is the initial concentration of the substance undergoing change. In general, the rate of change increases quickly with the concentration up to about $0.1N$ and very slowly afterwards. Assuming that the enzymes combine with the reacting substances, expressions may be obtained which represent the velocity very well, but this theory leaves out of account the colloidal nature of the enzymes. The application of Nernst's theory of reaction velocity in heterogeneous systems leads to absurdly large values for the thickness of the film surrounding the colloidal particles. The empirical formula for the initial velocities above mentioned is similar to that which represents the absorption of dissolved substances by colloids. This suggests that the substance is first absorbed by the colloid with a certain velocity, and that the change takes place within the colloid or at its surface. The velocity of change would then depend on the concentration within the colloid phase and on the rate of absorption. Experimental results on the hæmolysis of blood corpuscles by hæmolysins appear to support the last view. T. E.

The Solution State. W. PORTER DREAPER (*Chem. News*, 1905, 92, 229—232).—Regarding molecular and atomic forces as the same force differing in degree, it is suggested that the phenomena met with in solutions of crystalloids in colloids can be better explained on the balance between these two forces than by the assumption either of "hydrated" ions or of the isolation of ions in a negative medium. Conductivity is regarded as the result of "linking up" of solution and solute molecules; non-conductivity as a result of "grouping," as seen in pseudo-solutions. D. A. L.

Adsorption of Water Vapour and of Certain Salts in Aqueous Solution by Quartz. LYMAN J. BRIGGS (*J. Physical Chem.*, 1905, 9, 617—640).—The experiments were performed mainly with a view to investigating the causes of the retention of soluble substances by soils, and indicate that so far as quartz is concerned adsorption is of very minor importance in this respect. The surface of the quartz was estimated from the sizes of the particles, so that the results could be expressed in comparable units. With normal salts, no appreciable adsorption was found; the adsorption of the hydroxides is greater than that of the carbonates and is almost independent of the contained metal. In an $N/10$ solution of potassium hydroxide, the adsorption was about 0.6 mg. per square metre. It was found that quartz has the power of condensing a water film upon its surface, a portion of which only is removed by exposure to phosphoric oxide at the ordinary temperature. The remainder is only got rid of by heating to about 110° . In this case, the condensation cannot be ascribed to the presence of soluble substance on the surface of the solid, but is, in

the author's opinion, due to the attraction of the solid for the molecules of the vapour. The thickness of the temporary film is calculated as 4.5×10^{-7} cm.

L. M. J.

The Constitution of Crystalline Substances. FRÉDÉRIC WALLERANT (*Compt. rend.*, 1905, 141, 768—770).—In order to include soft or flexible crystals such as those of ammonium nitrate, and liquid crystals such as those of *p*-azoxyanisole (compare Schenck and Eichwald, *Abstr.*, 1904, i, 118), the phenomenon of crystallisation is explained as follows: the constituent particles of the substance exercise on one another two kinds of action, one of orientation and one of attraction; when the latter is strong, the particles assume fixed positions, arranging themselves in a network, and the crystalline substance is solid; when the power of attraction is weak, the particles have no fixed position, they are orientated in parallel directions, and the substance is liquid. In the intermediate cases, if the conditions are favourable to crystallisation, the particles may arrange themselves like the meshes of a sieve, and the crystals thus formed will remain malleable and be limited by plane faces, but if the conditions are less favourable, the sieve-like arrangement of the particles will be imperfect and the crystals will not present plane faces, as in the case of ammonium nitrate.

M. A. W.

New Triangle for Crucibles. ALFRED KETTE (*Chem. Zeit.*, 1905, 29, 1208—1209).—The "triangle" consists in the alternate arrangement around a circle of three circular arcs and three prisms of equilateral cross section, all of which are made of fire-resisting material. The six pieces are held together by a band of iron which passes round their outer circumference. The apices of the prisms, which project into the annular spaces in the centre, form the points of support for the crucible.

P. H.

Apparatus for Fractional Distillation under Constant Pressure. PETRU PONI (*Ann. sci. Univ. Jassy*, 1905, 3, 219—221).—The receiver of the usual apparatus for fractional distillation is provided with three necks; one is attached to the condenser; a second at the bottom, provided with a stopcock, serves for the withdrawal of the fractions; the third, also provided with a stopcock, communicates with an air-reservoir of ten to twelve litres capacity. The reservoir, which communicates with the atmosphere by a tube *f*, is also in connection with a calibrated U-tube mercury manometer. The pressure inside the apparatus is brought to 760 mm. by withdrawing or introducing air through the tube *f* until the difference of the levels of the mercury in the manometer is equal to the difference between the normal and the actual heights of the barometer. The stopcock on the tube *f* is then closed and the distillation performed.

A similar arrangement can be employed to determine boiling points under normal pressure.

C. S.

Inorganic Chemistry.

The Density of Chlorine Gas. FREDERICK P. TREADWELL and W. A. K. CHRISTIE (*Zeit. anorg. Chem.*, 1905, 47, 446—454).—The measurements were made by a method described by Bunsen. Two bulbs of equal capacity, and of approximately equal weight, were filled at constant temperature with chlorine and air respectively, and the difference of weight determined; the density of air being known, the density of chlorine can then be calculated readily. The chlorine, prepared from potassium dichromate and hydrochloric acid and carefully purified, still contained a small proportion of air, for which a correction was applied.

As a mean of three determinations at 20° and 730 mm., the value 2.488 (air = 1) was found, and two determinations at 10° and 725 mm. gave the value 2.489; according to Moissan and Binet du Jassoneix (*Abstr.*, 1904, ii, 114), the density at 0° and 760 mm. is 2.490. G. S.

Action of Hydrochloric Acid on Potassium Chlorate. A. KOLB (*Zeit. angew. Chem.*, 1905, 18, 1693—1694).—Polemical (compare Ditz, *Abstr.*, 1905, ii, 760; Kolb and Davidson, *ibid.*, 59).

H. M. D.

The System: Bromine and Iodine. P. C. E. MEERUM TERWOGT (*Zeit. anorg. Chem.*, 1905, 47, 203—243).—The freezing-point and boiling-point curves of mixtures of bromine and iodine have been determined, and vapour pressure and specific gravity measurements have been carried out, chiefly with the object of deciding whether a compound ICl exists in the solid, liquid, and gaseous systems.

Mixtures containing 50 atom. per cent. of each element solidify at constant temperature, but with mixtures in any other proportion the temperature falls a few degrees from the commencement to the completion of solidification; this indicates, according to Roozeboom's theory, the existence of a compound ICl , which, when the elements are present in other than equivalent proportions, separates out in mixed crystals with bromine or iodine.

The boiling-point curve was constructed by finding the initial boiling points of the various mixtures, and the composition of the vapour at these temperatures, and then plotting the composition of the liquid both against the initial boiling points and the boiling points of the evolved vapour on the same diagram. The two curves bend towards each other when the two elements are present in equivalent proportions, which may indicate the presence of ICl in a highly dissociated state. The boiling point of pure iodine is 188—189°.

The vapour pressure curve of the system was investigated by a static method up to 58 atom. per cent. iodine at 50.2°, and up to 80 atom. per cent. at 92.8°; larger proportions could not be employed owing to the formation of mixed crystals. The pressures were plotted

both against composition of liquid and of vapour; the resulting curves deviated considerably from a straight line. An attempt was made, according to a method suggested by van Laar (*Zeit. physikal. Chem.*, 1904, 47, 129), to deduce from the extent of this deviation whether ICl exists in the liquid and vapour phases, and the extent of its dissociation, but the results are not very conclusive.

The specific gravities of liquid and solid mixtures up to 58 atom. per cent. iodine were determined and plotted against the composition. The curves (except in the change from liquid to solid) are continuous, but deviate from a straight line, showing contraction; this may indicate formation of ICl or may arise from a physical cause.

The author concludes that ICl is present in the solid system; its existence in the liquid and vapour systems is probable, but not satisfactorily proved. G. S.

Iodic Acid. ERICH GROSCHUFF (*Zeit. anorg. Chem.*, 1905, 47, 331—352).—Besides iodic acid and iodine pentoxide, the existence of a crystalline substance of the formula $\text{I}_2\text{O}_5 \cdot \frac{1}{3}\text{H}_2\text{O}$ or HI_3O_8 has been proved by dehydration of iodic acid at different temperatures and by direct determination of the transition temperature. An amorphous modification of iodic acid is also described, which differs from the ordinary acid in being very hygroscopic. No hydrates of the acid could be obtained.

The complete solubility curve of iodic acid at different temperatures has been determined. The cryohydric point lies at -14° ; the mixture contains 72.7 per cent. of the acid. The transition temperature of iodic acid to the compound HI_3O_8 is at 110° ; the transition from the latter to the pentoxide takes place between 190° and 200° . The saturated solution boils at 111° under atmospheric pressure. The solution saturated at 18° contains about 295 grams of the acid to 100 grams of water, and has a sp. gr. of about 2.48. Strong solutions of the acid are very viscous, and it readily forms supersaturated solutions. The solubility of iodic acid in solutions of nitric acid of different strengths has also been determined.

Freezing-point determinations in aqueous solution show that the apparent molecular weight varies greatly with the concentration. In dilute (1 per cent.) solutions, the acid is present in single molecules which are highly ionised; in concentrated solutions, on the other hand, it seems to be polymerised, as suggested by Rosenheim and Liebknecht (compare *Abstr.*, 1899, ii, 743). This conclusion is confirmed by the results of electrical conductivity measurements; the degree of ionisation as calculated from freezing-point determinations agrees better with that deduced from conductivity measurements when the presence of complex molecules in concentrated solution is assumed. G. S.

Application of the Partial Liquefaction of Air with Reflux Action to the Complete Separation of Air into Pure Oxygen and Pure Nitrogen. GEORGES CLAUDE (*Compt. rend.*, 1905, 141, 823—826).—In a previous paper (*Abstr.*, 1904, ii, 23), the author described a method for separating the oxygen and nitrogen of air by

partial liquefaction; the separation was not, however, complete, as the final products contained only 92 per cent. of oxygen and 97—98 per cent. of nitrogen respectively. The present paper contains a description of a modification of the method whereby the separation is carried to completion. The apparatus consists essentially of a reservoir of liquid oxygen surmounted by a rectifying column; immersed in, but not communicating with, the liquid oxygen are two concentric coolers, each consisting of a small reservoir communicating with a series of vertical tubes. The air, cooled and compressed, enters the inner cooler, where it undergoes partial liquefaction; the liquid phase, containing about 48 per cent. of oxygen, falls back into the inner reservoir, the gaseous phase, rich in nitrogen, is partially liquefied in passing through the vertical tubes of the outer cooler, and nearly pure liquid nitrogen collects in the outer reservoir; by allowing the contents of the two reservoirs to percolate through the rectifying column, the liquid rich in nitrogen entering the column from the top whilst the liquid rich in oxygen enters at a slightly lower level, the descending liquids effect a complete rectification of the ascending gases and pure liquid oxygen collects in the large reservoir, whilst pure gaseous nitrogen escapes from the top of the rectifying column.

M. A. W.

The Liquefaction of Air by Expansion with Performance of External Work. GEORGES CLAUDE (*Compt. rend.*, 1905, 141, 762—764).—A description of a modification of the apparatus employed in producing large quantities of liquid air under pressures of 25 to 40 atmospheres (compare *Compt. rend.*, 1902, 134, 1568; 1903, 136, 1659; Abstr., 1904, ii, 23; preceding abstract).

M. A. W.

Molecular State of Water; its Chemical Constitution and the Relative Value of the Two Valencies of the Oxygen Atom. LOUIS HENRY (*Bull. Acad. Roy. Belg.*, 1905, 377—393).—A theoretical paper in which the author quotes evidence in favour of the molecular association of water, the chemical identity of the two hydrogen atoms of the molecule, and the consequent equality of the two valencies of the oxygen atom (compare de Forcrand, Abstr., 1905, ii, 696).

M. A. W.

Formation of Hydrogen Peroxide at High Temperatures. WALTHER NERNST (*Zeit. Elektrochem.*, 1905, 11, 710—713).—The formation of hydrogen peroxide cannot be observed when a mixture of steam and oxygen is passed through a hot platinum or iridium tube and then rapidly cooled. As this is possibly due to the great velocity with which the decomposition of hydrogen peroxide takes place, experiments on the rate of decomposition were made by passing a current of air containing a known quantity of hydrogen peroxide through a heated glass tube and then cooling it rapidly. The quantity of undecomposed hydrogen peroxide was estimated by adding a solution of titanium dioxide in concentrated sulphuric acid and measuring the absorption of light at the blue end of the spectrum by means of the spectro-photometer. It appears that the reaction is bimolecular, $2\text{H}_2\text{O}_2 \rightleftharpoons 2\text{H}_2\text{O} + \text{O}_2$, and that its velocity constants are very nearly the

same as those of the decomposition of ozone (Abstr., 1904, ii, 479). Hydrogen peroxide is not formed when electric sparks pass through a mixture of oxygen and water vapour (this is evidence in favour of the view that the formation of ozone is due to ultra-violet light); it is formed, however, when sparks are passed through liquid water, the rate of cooling being then sufficiently great to prevent its complete decomposition. T. E.

Chemical Oxydases acting in the Presence of Hydrogen Peroxide. G. BAUDRAN (*Compt. rend.*, 1905, 141, 891—892. Compare Abstr., 1905, ii, 407, 632).—Chlorates, bromates, iodates, and the alkali hypochlorites hypobromites, hypiodites, phosphates, and sulphates give a yellowish-green colour and precipitate with a 1 per cent. solution of guaiacol in the presence of hydrogen peroxide, the colour becoming red on the addition of hydrochloric or sulphuric acid; the salts of the aliphatic and aromatic acids give a similar reaction, which is accelerated by the addition of a small quantity of mercuric iodide solution. M. A. W.

Preparation of Colloidal Solutions of Selenium and Sulphur by Electrical Pulverisation. ERICH MÜLLER and ROMUALD NOWAKOWSKI (*Ber.*, 1905, 38, 3779—3781. Compare Müller and Lucas, Abstr., 1905, ii, 672; Gutbier, Abstr., 1902, ii, 652).—A colloidal solution of selenium is prepared by the electrical pulverisation in pure water of a cathode prepared by fusing a small piece of selenium on to platinum foil. This takes several hours with an *E.M.F.* of 20 volts, or is effected more quickly with a greater *E.M.F.* The hydrogen selenide formed with an *E.M.F.* of 20 volts is oxidised by the anodic and atmospheric oxygen; but with an *E.M.F.* of 220 volts, hydrogen selenide is evolved. The colloidal solution is fiery yellowish-red in thick layers, or a dirty yellow in thin layers, by transmitted, or yellowish-red by reflected light, and deposits selenium only slowly, except on the addition of an electrolyte.

A milky-white, colloidal solution of sulphur, having a strong odour of hydrogen sulphide, is formed by the cathodic pulverisation of a sulphur-platinum electrode, in pure water, with an *E.M.F.* of 220 volts. G. Y.

Preparation of Nitrogen from the Atmosphere. GEORGE A. HULETT (*J. Amer. Chem. Soc.*, 1905, 27, 1415—1418).—The following method is described for the preparation of nitrogen from the air. In a piece of combustion tubing of not less than 2 cm. diameter is placed a roll of copper gauze, 20 cm. long, followed by a layer of copper oxide of the same length. The tube is heated in a combustion furnace, both the copper and copper oxide being maintained at a red heat. Air and hydrogen are led directly into the tube and allowed to mix just before reaching the hot copper. The resulting gases are passed through solution of potassium hydroxide in order to remove the carbon dioxide. For details of the method, the description and diagram in the original must be consulted. E. G.

Atomic Weight of Nitrogen [and Silver]. PHILIPPE A. GUYE (*Arch. Sci. phys. nat.*, 1905, [iv], 20, 351—380).—A detailed account and discussion of work previously abstracted (*Abstr.*, 1904, ii, 557; 1905, ii, 442, 506, 702). The value 14·009 for the atomic weight of nitrogen appears to be completely confirmed, and the effect of this alteration is discussed. Three atomic weights are regarded as correct to 1 in 10,000, namely, C = 12·002, H = 14·009, and H = 1·0076. From these the author revises the value of atomic weight of silver, from the ratio Ag | AgNO₃ the value 107·882 is obtained, from Ag | CH₃·CO₂Ag 107·886, and from Ag | C₇H₅O₂Ag 107·888, with mean 107·885. From the ratios of Ag | NH₄Cl and Ag | Cl, employing Dixon and Edgar's value for chlorine, 35·463 (*Abstr.*, 1905, ii, 696), the numbers 107·871 and 107·895 are obtained; other values are: Ag₂ | Ag₂S, 107·884; Ag | AgO₂, 107·928; Ag₃ | Ag₃PO₄, 107·888, with a general mean of 107·885, and the author considers it certain, therefore, that it does not exceed 107·89. The lowering of this atomic weight will affect numerous other values. L. M. J.

Oxidation of Ammonia by Alkali Persulphates in Alkaline Solution. R. KEMPF (*Ber.*, 1905, 38, 3972—3974. Compare Marshall, *Abstr.*, 1901, ii, 156).—The ammonium salts contained in commercial sodium persulphate are oxidised to nitric acid (some 88 per cent.) when the solution in sodium hydroxide is kept for four days at about the ordinary temperature. When the solution is boiled, a considerable portion (some 40 per cent.) is oxidised to nitrogen. J. J. S.

Hydroxylamine and its Salts. W. H. ROSS (*Proc. Trans. Nova Scotian Inst. Sci.*, 1905, 11, 95—114).—A number of hydroxylammonium salts have been prepared and examined. Hydroxylammonium sulphate melts at 163° with decomposition; when heated above the melting point, it breaks up according to the equation $3(\text{NH}_3\cdot\text{OH})_2\text{SO}_4 = (\text{NH}_4)_2\text{SO}_4 + 2\text{SO}_2 + 2\text{N}_2\text{O} + 8\text{H}_2\text{O}$.

Hydroxylammonium chloride melts at 157°, and the molten substance decomposes according to the equation $3\text{OH}\cdot\text{NH}_3\text{Cl} = \text{NH}_4\text{Cl} + 2\text{HCl} + \text{N}_2 + 3\text{H}_2\text{O}$.

Hydroxylammonium phosphate is only moderately soluble in cold water, but readily forms supersaturated solutions. When heated in a vacuum, it decomposes according to the equation $2(\text{NH}_3\cdot\text{OH})_3\text{PO}_4 = 6\text{NH}_2\cdot\text{OH} + \text{H}_2\text{O} + \text{H}_4\text{P}_2\text{O}_7$. In an open vessel it decomposes at 148° into ammonia, water, phosphoric acid, ammonium phosphate, and nitrous oxide.

Hydroxylammonium nitrate is a viscid, colourless liquid which decomposes slowly at 80°, more rapidly at higher temperatures, with the formation of nitric acid, water, ammonium nitrate, nitrous and nitric oxides. It was obtained by distilling its aqueous solution under a pressure of 20 mm. and drying the distillate over phosphoric oxide.

The estimation of hydroxylamine by titration with iodine in presence of disodium phosphate (compare Haga, *Trans.*, 1887, 51, 794) was found to be unsatisfactory. The amount of iodine used increases considerably

when the quantity of disodium iphosphate present is increased, but is almost independent of the dilution.

The electrical conductivity of aqueous solutions of the free base and its salts was measured. The following numbers express the equivalent conductivity ($\mu \times 10^7$) at 18° in terms of mercury, v being the volume per gram-molecule of salt.

$v =$	2.	5.	10.	20.	50.	100.	200.	500.	1000.	2000.	5000.	10,000
Hydroxylamine ...	—	0.4	0.5	0.7	0.9	1.2	1.5	1.9	2.2	—	—	—
$\text{OH} \cdot \text{NH}_2\text{Cl}$	73.3	80.5	86.6	90.9	95.8	98.9	101.5	104.6	107.6	109.9	111.6	112.4
$\text{OH} \cdot \text{NH}_2\text{NO}_3$	—	—	106.7	112.6	119.1	122.3	124.7	127.1	129.8	131.8	134.0	135.5
$(\text{NH}_3 \cdot \text{OH})_2\text{SO}_4$...	—	63.8	71.6	80.5	92.0	97.7	103.0	109.3	113.0	115.9	118.9	120.3
$(\text{NH}_3 \cdot \text{OH})_2\text{PO}_4$...	—	19.8	22.0	23.6	24.7	25.5	26.0	26.4	26.6	26.8	27.0	27.1

The nitrate has a greater conductivity than the chloride, which is not what would be expected from a comparison with the salts of the alkali metals.

In all cases the conductivity of the salt solutions was found to increase with time, especially with the more dilute solutions. This is due to the decomposition of the salts under the influence of the platinum black of the electrodes; with polished electrodes, the effect is considerably smaller. The base itself is oxidised even more rapidly than the salts.

These phenomena necessitated special care in the determination of the conductivity data, and the values for solutions of the base are only regarded as approximate. H. M. D.

Density of Nitric Oxide; Atomic Weight of Nitrogen. PHILIPPE A. GUYE and CH. DAVILA (*Compt. rend.*, 1905, 141, 826—828. Compare Abstr., 1904, ii, 475, 557, 812; 1905, ii, 442, 506).—Owing to the discrepancies between the values obtained for the density of nitric oxide (air=1), 1.041 (Thomson), 1.0888 (Bérard), 1.094 (Davy), 1.1887 (Kirwan), and 1.0388 (Leduc), the authors have redetermined the constant, using nitric oxide prepared by three distinct methods: (1) decomposition of sodium nitrate or nitrite by mercury in sulphuric acid solution, (2) reduction of nitric acid or sodium nitrite by ferrous sulphate, or (3) decomposition of a dilute solution of sodium nitrite by sulphuric acid; it was purified by passing it through concentrated sulphuric acid, and subsequent repeated fractional liquefaction by means of liquid air. The mean of fourteen determinations of the weight of a litre of nitric oxide at N.T.P. is 1.3402 grams, the limiting values being 1.3408 and 1.3398 respectively, and is identical with the value recently found by Gray (*Trans.*, 1905, 87, 1601), who prepared his nitric oxide by the reduction of sodium nitrite by potassium ferrocyanide and acetic acid, and purified it by treatment with potassium hydroxide and final liquefaction and fractional distillation. The atomic weight of nitrogen calculated from the ratio of the densities of the gases NO/O_2 lies between 14.010 and 14.006 ($\text{O} = 16$). M. A. W.

Nitrosyl Fluoride. OTTO RUFF and KURT STÄUBER (*Zeit. anorg. Chem.*, 1905, 47, 190—202. Compare Moissan, Abstr., 1905, ii, 518).—With the object of obtaining a compound of nitrogen and fluorine,

Gore's experiments (this Journal, 1869, **22**, 391, 393) with nitric and hydrofluoric acids and with nitric acid, sulphuric acid, and sodium fluoride were repeated, and the action of nitrosylsulphuric acid on sodium fluoride was also investigated, in each case with negative results. It was found, however, that by the action of nitrosyl chloride on silver fluoride a gaseous substance was formed which proved to have the formula NOF.

The following method for preparing nitrosyl fluoride was found to give satisfactory results. A flask containing nitrosyl chloride, kept at -5° , was attached to one end of a long platinum tube containing silver fluoride and kept at $200-250^{\circ}$; the other end of the tube was connected with a small platinum flask provided with two stopcocks and cooled by liquid air. The nitrosyl chloride distilled slowly over the silver fluoride and the nitrosyl fluoride, along with unaltered chloride, was condensed in the platinum flask and purified by fractional distillation.

Nitrosyl fluoride is a colourless gas condensable to a colourless liquid, which boils at -56° and solidifies on further cooling to a colourless mass melting at -134° . In the cold, silicon, boron, red phosphorus, and sodium take fire in the gas, and arsenic and antimony are also immediately acted on, fluorides being formed in each case and nitric oxide evolved. Lead, aluminium, bismuth, and copper are only slowly acted on, whilst iodine, sulphur, and carbon are not affected even on heating. Nitrosyl fluoride is decomposed by water with formation of nitrous and hydrofluoric acids; it gives brown fumes in moist air. Both in physical and chemical properties it closely resembles the nitryl fluoride, NO_2F , isolated by Moissan, but differs from the latter in its behaviour towards water and iodine.

The formula NOF is confirmed by analysis and vapour density determinations. G. S.

Preparation of Phosphorus Di-iodide. HOWARD W. DOUGHTY (*J. Amer. Chem. Soc.*, 1905, **27**, 1444—1445).—A mixture of 50 grams of iodine and 4 grams of red phosphorus in a 250 c.c. flask is heated with a free flame until completely melted. When the product has cooled to 60° , 2.5 grams of yellow phosphorus are added in small pieces. By this method, phosphorus di-iodide can be safely and rapidly prepared. E. G.

Production of Carbon (Lampblack and Graphite) from Acetylene and Metallic Carbides. ADOLPH FRANK (*Zeit. angew. Chem.*, 1905, **18**, 1733—1735).—When acetylene under a pressure of five or six atmospheres is exploded, the charcoal (lampblack) obtained is contaminated with oily products resulting from the simultaneous partial condensation of the acetylene. If the acetylene is mixed with carbon monoxide or carbon dioxide in proportions given by the equations $\text{C}_2\text{H}_2 + \text{CO} = 3\text{C} + \text{H}_2\text{O}$ and $2\text{C}_2\text{H}_2 + \text{CO}_2 = 5\text{C} + 2\text{H}_2\text{O}$, these condensation products are not formed. The pressure of the mixture of acetylene and carbon monoxide before explosion should be at least six atmospheres; with this initial pressure value, the maximum pressure developed during the explosion amounts to 40—50 atmospheres. On

account of the high temperature developed, the reaction is not complete, but 85 per cent. of the theoretical quantity of carbon is obtained. The charcoal so produced has a high specific gravity—1.93 to 2.0—and its electrical conducting power is considerably greater than that of other forms of charcoal. It is very finely divided, very black, and has a high covering power.

When calcium, strontium, or barium carbide is heated in a current of carbon monoxide or dioxide, carbon separates in the form of graphite according to the equation $\text{CaC}_2 + \text{CO} = \text{CaO} + 3\text{C}$. Graphite is also obtained when the carbides are heated in a current of chlorine, phosphorus, or arsenic, but in these cases the yield is considerably less than the theoretical. The graphite obtained from calcium carbide and carbon monoxide leaves only about one per cent. of ash on combustion, is very hard, and has a high sp. gr. (2—2.05). It is eminently suitable for electrotechnical and electrochemical applications.

H. M. D.

Attempt to Liquefy Helium. KARL OLSZEWSKI (*Bull. Acad. Sci. Cracow*, 1905, 407—411. Compare Abstr., 1897, ii, 31; Dewar, Abstr., 1901, ii, 597; Travers, Senter, and Jaquerod, Abstr., 1903, ii, 9).—Helium, obtained by heating thorianite with potassium hydrogen sulphate, contained as impurity only nitrogen, which was removed completely by two coolings with liquid hydrogen. The helium so purified was cooled to -252.5° by boiling hydrogen, and then to -259° by hydrogen solidifying under 50 mm. pressure, and subjected to a pressure of 180 atmospheres, which was reduced slowly or suddenly to 1 atmosphere, when the gas showed no signs of liquefaction or the deposit of any solid, the temperature being lowered to -271.3° . The boiling point of helium is therefore below -271° or $+2^\circ$ absolute.

G. Y.

Coloration of the Halogen Salts of the Alkalis and Alkaline Earths. LOTHAR WÖHLER and H. KASARNOWSKI (*Zeit. anorg. Chem.*, 1905, 47, 353—370. Compare Abstr., 1901, ii, 166; Giesel, Abstr., 1897, ii, 170; Borchers and Stockem, Abstr., 1903, ii, 19).—Many naturally-occurring halogen compounds, such as rock-salt and fluor-spar, are coloured in various ways, and similar colours can be produced by exposing the colourless salts to the vapours of metals or to cathode rays. The origin of these colours has not been satisfactorily elucidated.

With the object of throwing light on this question, the authors heated natural blue rock-salt and colourless pieces of the same substance in a stream of oxygen, and found that both specimens contained about 0.016 per cent. of carbon and 0.008 per cent. of hydrogen, indicating the presence of traces of organic matter. For comparison, artificially coloured specimens of several halogen salts have been prepared by heating the crystals in the vapour of different metals, and it was found that under these conditions the halogen salts of the alkali metals became deeply coloured in fifteen minutes, and the colour did not deepen on further heating. Excess of metal could not be detected in these salts by chemical analysis, so that the amount

present must be very small. On the other hand, a specimen of fluor-spar, blue by transmitted and green by reflected light, prepared by heating colourless crystals of the salt in calcium vapour, was found on analysis to contain 2.4 per cent. of the metal in excess. Attempts to prepare coloured salts by electrolysis were not very successful; only those parts of the fused mass which were kept fairly cool were found to be coloured.

All the coloured salts referred to lose their colour when heated, but this change takes place at a much lower temperature in the case of the naturally coloured salts. Further, the latter are neutral in reaction, and the colour is unaffected by water, whereas the artificially coloured salts are alkaline and become decolorised on treatment with water. It seems likely that the coloration arises from different causes in the two cases; with artificially coloured salts, it is probably due to traces of metal or subchloride in solid solution in the halogen salt, in the other cases to traces of organic matter. The colour does not depend on the amount of foreign substance present, but chiefly on its mode of occurrence, as in coloured glasses.

The coloration produced by the vapours of metals and by cathode rays probably arises from the same cause.

G. S.

Sodium Hyposulphite. III. ARTHUR BINZ and W. SONDAG (*Ber.*, 1905, 38, 3830—3834. Compare Abstr., 1904, i, 964; 1905, ii, 521).—A method is described of estimating in the same solution hyposulphite, sulphate, thiosulphate, and sulphite. By this means it is possible to follow the changes which take place on mixing the hyposulphite with thiosulphate. The products are sulphite and sulphide.

$\text{Na}_2\text{S}_2\text{O}_4 + \text{Na}_2\text{S}_2\text{O}_3 + 4\text{NaOH} = 3\text{Na}_2\text{SO}_3 + \text{Na}_2\text{S} + 2\text{H}_2\text{O}$; in the actual experiment, 1.00 mol. $\text{Na}_2\text{S}_2\text{O}_4$ with 0.99 mol. $\text{Na}_2\text{S}_2\text{O}_3$ gave 2.92 mol. Na_2SO_3 and 1.00 mol. Na_2S .

T. M. L.

Lithium Alumino-silicates. Z. WEYBERG (*Centr. Min.*, 1905, 646—655. Compare Abstr., 1905, ii, 89, 98, 262).—By fusing kaolin ($\text{H}_2\text{Al}_2\text{Si}_2\text{O}_5, \text{H}_2\text{O}$) with potassium chloride, Gorgeu (1887) obtained the product $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$. This compound is, however, only obtained in the crystallised condition when an alkali carbonate is added to the mixture, or when the free bases and silica are used instead of kaolin. On the other hand, the more readily decomposed lithium salts, when fused with kaolin, give well-crystallised products. Thus, by fusing kaolin with lithium chloride or lithium carbonate, a white, crystalline powder is obtained, the crystals being orthorhombic and having the composition $\text{Li}_6\text{Al}_2\text{Si}_2\text{O}_{10}$. With lithium sulphate, the crystallised (orthorhombic) product has the composition $\text{Li}_2\text{Al}_2\text{Si}_2\text{O}_8$. With lithium bromide, a lithium bromo-sodalite, $7\text{Li}_2\text{Al}_2\text{Si}_2\text{O}_8, 2\text{LiBr}$, crystallising in rhombic dodecahedra, was obtained.

The kaolin used in the experiments had the following composition :

	SiO_2 .	Al_2O_3 .	H_2O .	Total.
From South Russia...	45.76	39.87	14.44	100.07
„ Meissen	49.41	37.06	13.53	100.00

L. J. S.

Lithium Chromates. FRANS A. H. SCHREINEMAKERS (*Chem. Centr.*, 1905, ii, 1486; from *Chem. Weekblad*, 2, 633—639. Compare Abstr., 1905, ii, 818, 820).—The only substances which can separate in a solid form from a system which consists of lithium oxide, chromic acid, and water at 30° are lithium hydroxide, $\text{LiOH}\cdot\text{H}_2\text{O}$, chromate, $\text{Li}_2\text{Cr}_2\text{O}_4\cdot 2\text{H}_2\text{O}$, dichromate, $\text{Li}_2\text{Cr}_2\text{O}_7\cdot 2\text{H}_2\text{O}$, and chromic acid, CrO_3 . Higher chromates than the dichromate cannot exist at 30°. A saturated solution of lithium hydroxide contains 7.09 per cent.; 100 parts of water dissolve 99.94 and 130.4 parts of lithium chromate, Li_2CrO_4 , and lithium dichromate, $\text{Li}_2\text{Cr}_2\text{O}_7$, respectively. The solubility of the chromates of ammonium, potassium, sodium, and lithium increases in the order given, whilst for the dichromates the order of solubility is potassium, ammonium, lithium, sodium.

E. W. W.

Decomposition of Ammonium Sulphate by Sulphuric Acid in the Presence of Platinum. MARCEL DELÉPINE (*Compt. rend.*, 1905, 141, 886—889).—The low results obtained when the nitrogen of platinichlorides is estimated by the Kjeldahl method (compare Abstr., 1895, ii, 290, and van Dam, Abstr., 1896, ii, 218) are due to the decomposition of the ammonium sulphate with loss of nitrogen, for if spongy platinum or platinum foil is boiled with sulphuric acid containing ammonium sulphate, sulphur dioxide is formed and nitrogen is evolved, the quantity increasing with the duration of heating, the temperature, and the addition of potassium sulphate. It is probable that the platinum acts as a catalyst, the sulphate being first formed and then decomposed by the ammonium sulphate according to the equations: (1) $4\text{H}_2\text{SO}_4 + \text{Pt} = \text{Pt}(\text{SO}_4)_2 + 2\text{SO}_2 + 4\text{H}_2\text{O}$; (2) $3\text{Pt}(\text{SO}_4)_2 + 2(\text{NH}_4)_2\text{SO}_4 = 2\text{N}_2 + 3\text{Pt} + 8\text{H}_2\text{SO}_4$, for the solution obtained by boiling platinum in sulphuric acid deposits platinum when heated with ammonium sulphate, and, further, when the platinum in the above experiment is replaced by gold or iridium, which is not attacked by sulphuric acid, there is no loss of nitrogen.

M. A. W.

Separation of Constituents of Alloys. A. BOCK (*Chem. Zeit.*, 1905, 29, 1199—1201).—The introduction of a third metal into a molten alloy of two metals causes a partial separation of the two constituents and a consequent loss of homogeneity in the resulting mass on solidification. The extent of the disturbance is less in thin layers of the alloy than in large blocks. The Pattinson desilverising process is attributed to the influence of the iron of the containing vessels on the molten alloy of lead and silver. The author also attributes to the iron of the mould in which they are cast the segregation observed with certain silver-copper and gold-silver alloys.

P. H.

Oxidations with Silver Peroxide. I. Oxidation of Oxalic Acid. R. KEMPF (*Ber.*, 1905, 38, 3963—3966).—Silver peroxide is formed when solutions of silver nitrate and potassium persulphate are mixed (Marshall, Trans., 1891, 59, 771). Such a mixture is capable of oxidising numerous carbon compounds. Quinone yields maleic acid

and carbon dioxide together with formic acid and carbon monoxide. Oxalic acid can be quantitatively oxidised to carbon dioxide.

A simple lecture experiment may be conducted as follows: 5 c.c. of a 10 per cent. silver nitrate solution are added to a mixture of 20 grams of ammonium persulphate in 100 c.c. of 10 per cent. sulphuric acid and 100 c.c. of *N*-oxalic acid. A slight precipitate of silver sulphate is formed, the solution becomes warm, and the evolution of gas is completed in a few minutes. The active oxygen of the persulphate may be estimated by mixing with excess of standard oxalic acid solution, adding dilute sulphuric acid containing a little silver sulphate, and titrating the excess of oxalic acid with permanganate. J. J. S.

Oxidations with Silver Peroxide. II. Formation of Nitric Acid from Ammonium Persulphate. R. KEMPF (*Ber.*, 1905, 38, 3966—3971. Compare Marshall, *Abstr.*, 1901, ii, 156).—When silver sulphate is added to a solution of ammonium persulphate in dilute sulphuric acid, a brown precipitate of silver peroxide is formed, but this disappears in the course of several days, practically no oxygen is evolved, the persulphate is destroyed, and nitric acid is produced. The reaction proceeds but slowly, for example, 0.63 gram of ammonia (as ammonium salt) required forty-eight hours. In the absence of silver salts, persulphates are not able to bring about the oxidation, which must be due to silver peroxide and not to ozone, Caro's acid, or hydrogen peroxide. The oxidation is not quantitative. J. J. S.

Electrolytic Calcium. JOSEPH H. GOODWIN (*J. Amer. Chem. Soc.*, 1905, 27, 1403—1415).—A method is described for the preparation of calcium by the electrolysis of fused calcium chloride. A hollow cylindrical vessel of Acheson graphite is employed as the anode and an iron rod as the cathode. With a current of 163 amperes, about 17.7 volts are required, the current efficiency being 29.1 per cent. For details of the apparatus, reference must be made to the description and diagrams in the original paper.

The bright metal obtained by this method was found to contain 98.0 per cent. of calcium, had a sp. gr. 1.5446 at 29.2°, a specific electrical resistance of 3.43 microhms per c.c. at 0°, and a tensile strength of 612 kilograms per sq. cm. Calcium is harder than sodium, lead, or tin, nearly as hard as aluminium, but softer than zinc, cadmium, or magnesium. E. G.

Composition of Metallic Calcium. B. LARSEN (*Chem. Centr.*, 1905, ii, 1466; from *Mitt. Techn. Gewerb.-Mus. Wien*, [ii], 15, 244—246).—A sample of metallic calcium from the Electrochemical Works in Bitterfeld has been found to contain 99.64 per cent. of calcium, 0.2 of iron, 0.09 of manganese, 0.06 of silica, and 0.11 of calcium carbide. The metal was broken on an anvil and the manganese may possibly have been derived from the tool, which was made of manganese steel. The pieces, which weighed from 6—8 grams, were quickly immersed in naphtha so that the fresh surfaces scarcely became tarnished. After removing the naphtha from the sample for analysis by means of ether, the metal was dried in a stream of dry

air and finally dissolved in hydrochloric acid cooled by ice. The quantity of calcium carbide was determined by weighing the copper acetylide formed from the acetylene which was liberated.

E. W. W.

Tarugi's View of the Formation and Composition of Bleaching Powder. HUGO DITZ (*Zeit. angew. Chem.*, 1905, 18, 1690—1693. Compare Tarugi, *Abstr.*, 1905, ii, 32).—Tarugi's view that bleaching powder is a substance of the formula $\text{CaO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$, corresponding with 44.09 per cent. of active chlorine, is inconsistent with the analyses of different samples of bleaching powder. On the assumption of this formula, the sum of the percentage numbers for the various constituents of three samples of bleaching powder examined amounts approximately to 110. The excess of this number over 100 corresponds almost exactly with 1 atom of oxygen.

H. M. D.

Revision of the Atomic Weight of Strontium. II. Analysis of Strontium Chloride. THEODORE W. RICHARDS (*Zeit. anorg. Chem.*, 1905, 47, 145—150).—In a previous investigation (*Abstr.*, 1895, ii, 314), the value $\text{Sr} = 87.663$ was found from the analysis of strontium bromide. In the present paper, the analysis of the chloride by a similar method is described; the ratio $\text{SrCl}_2 : 2\text{Ag}$ was found by titrating the carefully purified salt against silver dissolved in nitric acid, the end-point being determined by means of the nephelometer (compare *Abstr.*, 1904, ii, 287). When the value $\text{Cl} = 35.473$, found by Richards and Wells, is taken as the basis of calculation, the value $\text{Sr} = 87.661$ is obtained as the mean of four concordant experiments, in satisfactory agreement with the result obtained with the bromide, whilst there is a considerable difference when the former atomic weight of chlorine is employed. The new value for chlorine is thus confirmed.

The mean of the two series, $\text{Sr} = 87.662$ ($\text{O} = 16$), may be taken as the most probable value.

G. S.

Barium Oxide and its Hydrates: the Preparation of a New Hydrate. O. BAUER (*Zeit. anorg. Chem.*, 1905, 47, 401—420).—The compound $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ melts at 78° and begins to boil at 103° ; on continued heating, the temperature rises steadily to 109° , at which point it remains constant for some time, and crystals of a hydrate, $\text{Ba}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, not previously described, separate out. The new hydrate occurs in clear, lustrous, rhombic crystals; chemically it behaves in all respects like the octahydrate.

Corresponding strontium and calcium compounds could not be obtained.

G. S.

Alloys of Cadmium and Zinc containing Lead. FRANZ NOVAK (*Zeit. anorg. Chem.*, 1905, 47, 421—445. Compare Ericson-Auren and Palmaer, *Abstr.*, 1902, ii, 64; Brunner, *Abstr.*, 1904, ii, 315; 1905, ii, 235).—The investigation was undertaken with the object of determining how the properties of zinc on which its employment for process blocks depend are modified by small amounts of

cadmium and lead. The metal was used in the form of thin sheets, rolled at 120°. The precautions taken to secure uniformity of composition in the alloys are described.

The rate of solution in acids was determined by measuring the hydrogen evolved and by finding the loss of weight of the plates; it was found, in agreement with Spring (Abstr., 1888, 900), that the reaction velocity only attains its maximum value after some time (induction period). The rate at which zinc containing 0.1—0.8 per cent. of lead is dissolved by $N/10$ hydrochloric acid is lessened by the addition of cadmium up to 1 per cent., and the induction period is lengthened. On the other hand, the rate of solution in 5 per cent. nitric acid is somewhat increased by addition of cadmium. Quantities of lead up to 2 per cent. (the limit of solubility of this metal in zinc) have no effect on the reaction velocity, larger proportions lessen it considerably. These results find a simple explanation on the theory that the rate of solution is greatly influenced by local electric currents (compare Ericson-Auren and Palmaer, *loc. cit.*).

When zinc and its cadmium alloys are heated at 270° for some time and then cooled, they are attacked by acids rather more rapidly than samples which have been rolled at 120°; this behaviour is connected with a change in the crystalline structure.

Addition of $\frac{1}{4}$ per cent. of cadmium increases the hardness and breaking stress of zinc, but when more than $\frac{1}{2}$ per cent. of the former metal is present, the opposite effect is produced.

Photomicrographs of several of the alloys referred to are given in the paper. G. S.

Determination of Atomic Weights of Rare Earths. OTTO BRILL (*Zeit. anorg. Chem.*, 1905, 47, 464—476. Compare Nernst and Riesenfeld, Abstr., 1903, ii, 571).—Further experiments on the rare earths have been made with Nernst's micro-balance by the method already described (*loc. cit.*).

A method largely used in determining the atomic weights of rare earths is to convert the oxide into the corresponding normal sulphate or *vice versa*. According to Krüss (Abstr., 1893, ii, 283), acid sulphates are completely converted into normal sulphates by heating for some time at 350°. To test this method, oxides of several rare earths were evaporated with sulphuric acid, small quantities of the resulting acid sulphates placed in the scale pan of the micro-balance, and heated in an electric furnace for ten or fifteen minutes at temperatures increasing by intervals of 50°, the weight being determined after each heating. At 350°, the weight did not remain constant, so that, as Wild has also pointed out (Abstr., 1904, ii, 173), the temperature given by Krüss for conversion into the normal sulphate is too low. At 450°, the conversion to normal sulphate was complete, at 700° this began to decompose into basic sulphate, the change being complete at 900°; at 1150°, the latter was completely transformed into oxide. The basic sulphates of yttrium, ytterbium, erbium, lanthanum, and samarium, thus prepared for the first time, have the general formula, $M_2O_3 \cdot SO_3$, and occur in white needles. From the order in which they decompose on heating, the relative basic character of the oxides can be

determined; from the weakest to the strongest base the order is Yb, Er, Y, Sa, La.

It is shown that atomic weights can readily be determined by heating at 480° to form the normal sulphate, then at 1150° for some minutes to form the oxide; the method is particularly useful for rapidly determining the atomic weights of fractions. G. S.

Victorium, and the Ultra-violet Phosphorescence of Gadolinium. GEORGES URBAIN (*Compt. rend.*, 1905, 141, 954—958).—If the phosphorescent spectrum obtained by Crookes with different specimens of gadolinium (Abstr., 1899, ii, 751; 1905, ii, 250) is correctly ascribed to a new element, victorium, the intensity of the spectrum should be diminished by diluting the gadolinium. The author finds, however, that a mixture of 2.8 parts of gadolinium oxide and 97.2 parts of lime gives a phosphorescent spectrum in which the bands are very intense, and similar results are obtained with mixtures of lime containing only 2/10,000 parts of gadolinium oxide; it follows, therefore, that the phosphorescent spectrum given by gadolinium is a characteristic of that element itself. M. A. W.

Preparation of Crystalline Crocoite and Wulfenite by the Action of Atmospheric Carbon Dioxide on Alkaline Solutions of the Lead Salts. G. CESÀRO (*Bull. Acad. roy. Belg.*, 1905, 327).—Many insoluble lead salts dissolve in a solution of potassium hydroxide and these solutions, on slow neutralisation by atmospheric carbon dioxide, deposit the lead salts in a crystalline form. Such a solution of lead chromate, on exposure to the air for four months, gave a red, crystalline deposit which had the appearance and properties of crocoite. A solution of lead molybdate became turbid and blue, but after some time gave a very dense grey, granular powder with a metallic lustre, formed of microscopic, transparent, tetragonal tablets. F. G. C. S.

Distillation of Copper. HENRI MOISSAN (*Compt. rend.*, 1905, 141, 853—857. Compare Abstr., 1893, ii, 507; 1904, ii, 617; Féry, Abstr., 1903, ii, 293; Krafft and Bergfeld, Abstr., 1905, ii, 144).—Copper is readily distilled when heated in an electric furnace; with a current of 300 amperes and 110 volts, 77.7 per cent. of the metal is volatilised in eight minutes, whilst with a current of 800 amperes and 110 volts several kilograms of copper can be distilled in a few minutes. The metallic distillate condenses on a copper cooler placed in the furnace in the form of iridescent filaments 5 to 7 mm. thick, having a red to yellow colour, a sp. gr. 8.16 (Kalhbaum, Roth, and Siedler found 8.932, Abstr., 1902, ii, 259), and containing 99.76 per cent. of copper, the impurities consisting of lime and graphite. The fused ingot of copper remaining in the crucible exhibits the phenomenon of "spitting," on cooling evolving large quantities of gas, and when quite cold is covered with a layer of graphite having a sp. gr. of 2.12, and consisting of 96.25 per cent. of carbon, 3.36 per cent. of ash, and 0.21 per cent. of hydrogen. A microscopic

examination of a polished section of the ingot shows that it contains a large number of spherical cavities lined with brilliant crystals of graphite.
M. A. W.

Copper and Arsenic. K. FRIEDRICH (*Metallurgie*, 1905, 2, 477—495).—The author has studied the alloys of copper and arsenic containing 0—44 per cent. of arsenic. Alloys richer in arsenic than this cannot be obtained under atmospheric pressure, and the higher alloys lose most of their arsenic when heated for any length of time at 300°. The freezing-point curve shows a well-marked maximum at 70·88 per cent. As and 830°, corresponding with the compound Cu_3As , and the existence of a compound Cu_5As_2 , dissociating below its melting point, is also indicated. Eutectic points occur at 78·5, 60·6, and 52·5 per cent. of arsenic respectively, the corresponding eutectic temperatures being 683°, 711°, and 603°. A transformation of unknown character was observed at 307°. The microscopic examination of sections etched with copper ammonium chloride or electrolytically in dilute nitric acid confirms the evidence of the freezing-point curve.

The formation of Cu_6As and Cu_9As , occurring in nature as algodonite and whitneyite respectively, is not observed in melting together copper and arsenic, and the existence of the compound Cu_2As is also not confirmed.
C. H. D.

Commercial Cuprosilicon. PAUL LEBEAU (*Compt. rend.*, 1905, 141, 889—891. Compare Vigouroux, *Abstr.*, 1896, ii, 362, and Chalmot, *Abstr.*, 1896, ii, 362).—A microscopical examination of the polished surface of commercial cuprosilicon shows that it contains large and small crystals of silicon embedded in a matrix of cuprosilicon; when the uncombined silicon is removed by treatment with 10 per cent. sodium carbonate solution and the cuprosilicon dissolved in nitric acid, a residue is left consisting of steel-grey crystals of ferrosilicon, FeSi_2 , and these three constituents are present in the following proportions: free silicon 51·11, cuprosilicon 49·97, ferrosilicon 3·49 per cent. The cuprosilicon contains 10·36 to 10·88 per cent. of silicon, and has therefore the composition Cu_4Si , and not Cu_2Si as stated by Vigouroux (*Abstr.*, 1896, ii, 362) and de Chalmot (*Abstr.*, 1896, ii, 362; 1897, ii, 262).
M. A. W.

A Modification of Mercurous Chloride. JULIUS MEYER (*Zeit. anorg. Chem.*, 1905, 47, 399—400).—When solutions of mercuric chloride and lithium sulphite are mixed, the heavy, white precipitate of ordinary calomel filtered off, and the clear solution heated to 70—80°, a new modification of mercurous chloride separates in lustrous scales. It has a sp. gr. 4·5—5 as compared with 6·5—7 for the ordinary salt; it changes into the latter on sublimation. It shows no difference of potential when measured against ordinary mercurous chloride in a galvanic cell, so that it does not seem to be an allotropic modification of the latter.
G. S.

Action of Silicon on Pure Aluminium and its Action on Impure Aluminium. Silicoaluminides. ÉMILE VIGOUROUX (*Compt. rend.*, 1905, 141, 951—953).—Pure silicon and aluminium do not combine to form an aluminium silicide, but when heated in the presence of the oxide or a salt of another metal, a compound containing silicon, aluminium and the metal, or the *silicoaluminide* of the metal is formed. The silicoaluminides of iron, nickel, cobalt, chromium, manganese, molybdenum, tungsten, vanadium, uranium, and titanium have been prepared; they are crystalline, hard, dense, brittle, and present a metallic appearance. A few are attacked by dilute acids with formation of silica, but most of them resist the action of even concentrated acids with the exception of hydrofluoric acid, and they are not attacked by solutions of alkali hydroxides.

M. A. W.

Physical and Chemical Properties of Slags. THOMAS TURNER (*J. Soc. Chem. Ind.*, 1905, 24, 1142—1147).—The classification of slags, their physical properties, the crystallisation, melting points, temperatures of formation, and fluidity are discussed. Experiments have been undertaken to ascertain as far as possible the constitution of a typical slag. A quantity of blast furnace slag weighing six tons was allowed to cool slowly, and samples were taken from six positions chosen so as to represent the relative order of solidification. No evidence of the separation of calcium or aluminium silicates during the process of cooling is afforded by the analytical data for the various samples. The most noteworthy fact elucidated is that the last fluid portion, which had a creamy-white colour, contained a distinctly smaller proportion of sulphur than the other samples. Apart from this elimination of sulphur from the liquid portion of the slowly cooling slag, there is but little evidence of any alteration in composition. The proportion of aluminium is, however, highest in the parts which contain most sulphur, and these parts have the most marked blue colour. This observation supports the view that the blue colour of the blast furnace slag is due to some form of aluminium oxysulphide. With regard to the relationship of magnesium and sulphur, the sample richest in sulphur contained the smallest proportion of magnesium and *vice versa*.

Cooling curves of the different samples were taken, but these give no evidence of eutectics, and do not permit of a distinction between the fluid, plastic, and solid states. Solidification extends over a wide temperature interval, but very different values were obtained by different observers for the temperatures at which the process begins and ends.

H. M. D.

Volatility of Indium Oxide. JULIUS MEYER (*Zeit. anorg. Chem.*, 1905, 47, 281—286).—The determination of the atomic weight of indium by conversion into the oxide is inaccurate owing to the volatility of the latter at high temperatures. It is shown in the present paper, however, that the loss of weight on heating the oxide for several hours in a specially constructed platinum crucible at 1100° is inappreciable. In the conversion of indium nitrate into oxide by

ignition, a constant weight cannot be attained even at 1100° ; this seems to be due to the obstinate retention of oxides of nitrogen by the oxide. The difficulty can be obviated to some extent by repeatedly treating the oxide with water and evaporating, or by converting the nitrate into hydroxide with ammonia and subsequently igniting.

G. S.

Interaction of Hydrochloric Acid and Potassium Permanganate in the Presence of Various Inorganic Salts. JAMES BROWN (*Zeit. anorg. Chem.*, 1905, 47, 314—330. Compare Abstr., 1905, ii, 166).—Standard solutions of hydrochloric acid and of potassium permanganate were heated alone and with known amounts of various inorganic salts for a definite time at 50° , a definite amount of standard oxalic acid was then added and standard permanganate run in until the red coloration was permanent. In a former paper it was shown that the greater amount of permanganate apparently reduced in the presence of ferric chloride is not due to the catalytic action of the salt, as Wagner had supposed (Abstr., 1899, ii, 275), but to oxidation of part of the oxalic acid by the chlorine evolved during the action. Corresponding experiments with the chlorides of cadmium, chromium, gold, and platinum show a greater apparent reduction of permanganate in presence of these salts in agreement with Wagner, but when the chlorine is removed by a current of air before adding the oxalic acid, the apparent amount of reduction is not affected by the presence of cadmium and gold salts, but is increased by chromium and platinum salts. The author draws the conclusion that the chlorides of the three metals first mentioned have no catalytic effect on the action, the difference in the case of chromium being due to secondary reactions (partial oxidation to chromate), whereas platonic chloride acts as a catalyst.

Since the observed differences in the majority of cases are due to the disturbing action of the evolved chlorine, the latter must have less effect in the presence of salts; no very satisfactory explanation of this has been found. Direct experiments show that after digestion there is less chlorine present in solutions containing salts than in the others, but as no appreciable amount escapes into the air, the suggestion is made that in the former case it is used up in some secondary reaction.

The retarding effect of manganous salts on the reaction in question is probably due to the production of higher oxides of manganese in larger amount, so that more oxalic acid is required for complete reduction.

G. S.

Equilibrium Diagram of Iron-carbon Alloys. GEORGES CHARPY (*Compt. rend.*, 1905, 141, 948—951).—Roozeboom's equilibrium diagrams for iron-carbon systems (Abstr., 1900, ii, 728; 1904, ii, 717) were based on the cooling curves for iron-carbon mixtures obtained by Roberts-Austen by allowing the fused mixtures to cool rapidly; the author finds, however, that if, in the case of mixtures containing from 2 to 4 per cent. of carbon, the cooling is gradual, the two main branches of the cooling curve represent respectively the separation of mixed crystals and of cementite; at 1150° (not 1050° as is usually stated), the eutectic product consisting of mixed crystals and cementite

solidifies, and below that temperature cementite separates from the solid solution; whilst if the cooling is rapid, the eutectic product, which solidifies at $1160-1165^{\circ}$, consists of mixed crystals and graphite, mixed crystals or graphite separating above that temperature, and graphite separating from the solid solution below that temperature.

M. A. W.

Compounds of Iron with Silicon. W. GUERTLER and GUSTAV TAMMANN (*Zeit. anorg. Chem.*, 1905, 47, 163—179).—The authors have studied the freezing-point curve of alloys of iron and silicon, and have confirmed the conclusions thus arrived at by microscopic observations and in some cases by chemical analysis.

The curve falls rapidly from the freezing point of iron to a point at which 33 atom. per cent. of silicon is present; along this part of the curve mixed crystals of Fe and Fe_2Si separate out in the form of cubes. The alloy containing 33 atom. per cent. silicon solidifies at a constant temperature like a pure metal and may be made up of saturated mixed crystals or may be a definite chemical compound of the formula Fe_2Si ; the latter view is the more probable, since several previous investigators have isolated a compound of this formula by treating alloys poor in silicon with acids, but no other case is known in which a chemical compound is the last member of a series of mixed crystals. Beyond this point the curve falls slightly until at 34.7 atom. per cent. silicon it reaches the eutectic point of mixtures of Fe_2Si and a new compound FeSi at a temperature of 1235° . This descending part of the curve between 33.3 and 34.7 atom. per cent. silicon cannot be determined directly owing to the small temperature difference (about 8°); its existence is deduced from the microscopic observation that the alloy containing 34.7 atom. per cent. silicon is a eutectic mixture. Beyond 34.7 per cent. silicon, the curve rises to a well-defined maximum at a temperature of 1443° , when 50 atom. per cent. of each element is present corresponding with the compound FeSi ; along this part of the curve, crystals of FeSi , surrounded by masses of the eutectic mixture of Fe_2Si and FeSi , separate out. Beyond 50 atom. per cent. silicon, the curve falls until at 76 atom. per cent. the eutectic point of FeSi and silicon is reached at a temperature of 1245° ; it then rises to the melting point of silicon. Between 76 and 100 atom. per cent. silicon, long crystals of this element, surrounded by the eutectic Si, FeSi , separate out.

Hot potassium hydroxide rapidly attacks silicon, slowly acts on FeSi , and has practically no action on Fe_2Si and iron. Hydrochloric acid, on the other hand, acts rapidly on iron, slowly on Fe_2Si , and has scarcely any effect on FeSi and Si. These facts can be made use of in analysing the alloys.

The hardness of these substances decreases with increasing percentage of iron. Alloys containing up to 47.5 atom. per cent. silicon are magnetic, whilst those containing more than 50 atom. per cent. are non-magnetic. The transition temperature of α - into β -iron does not seem to be appreciably altered by the presence of silicon. G. S.

Action of Silicon Chloride on Iron. EMILE VIGOUROUX (*Compt. rend.*, 1905, 141, 828—830).—Silicon tetrachloride is completely

decomposed by iron below a red heat, or at 1100° with the formation of the iron silicide, Fe_2Si , and ferrous chloride according to the equation $\text{SiCl}_4 + 4\text{Fe} = \text{Fe}_2\text{Si} + 2\text{FeCl}_2$. Iron silicide, Fe_2Si , is decomposed by chlorine with incandescence, by concentrated hydrochloric acid, or by aqua regia; it dissolves completely in dilute hydrofluoric acid, and is not attacked by acetic or nitric acid (compare Moissan, Abstr., 1896, ii, 173; Lebeau, Abstr., 1900, ii, 729; 1901, ii, 317; and Jouve, Abstr., 1902, ii, 595). Attempts to prepare the higher silicide, FeSi , obtained by Frémy (*Enc. Chim.*, Art. *Fer.*), by the action of silicon tetrachloride on iron, were unsuccessful. M. A. W.

The Composition of Colloidal Ferric Hydroxychloride in Relation to the Concentration of Hydrochloric Acid in the Containing Fluid. G. MALFITANO (*Compt. rend.*, 1905, 141, 660—662, 680—683. Compare Abstr., 1905, ii, 459).—The colloid is obtained by heating a 0.5 per cent. solution of ferric chloride in an autoclave at 100 — 115° for fifteen to thirty minutes; after dialysis and filtration through collodion, a solid colloidal residue is obtained. A washed preparation contained 1.57 per cent. Fe and 0.16 per cent. Cl, and after dialysis a 0.01 per cent. solution of HCl.

It is concluded that the amount of HCl separating depends on the quantity and composition of the colloid and is proportional to the quantity of water and increases with rise of temperature, hence the system $\text{H}(\text{Fe}_2\text{O}_6\text{H}_6)_n\text{Cl}$ tends to exist in equilibrium with the solution in which it is suspended.

By the action of free hydrochloric acid on colloids of the type $\text{H}(\text{Fe}_2\text{O}_6\text{H}_6)_n\text{Cl}$, the value of n diminishes, $\text{H}(\text{Fe}_2\text{O}_6\text{H}_6)\text{Cl}$ being the limiting value; for instance, 25 c.c. of a preparation containing (in millionths of a gram atom) $1654\text{H}(\text{Fe}_2\text{O}_6\text{H}_6)_{3.2}\text{Cl} + 76\text{HCl}$ are filtered and heated with 200 c.c. containing 3464HCl , and after cooling and filtration analysis indicates $1828\text{H}(\text{Fe}_2\text{O}_6\text{H}_6)_{2.91}\text{Cl} + 3290\text{HCl}$.

From numerous similar experiments, the author concludes that on increasing the concentration of HCl the colloid approaches more nearly to $\text{H}(\text{Fe}_2\text{O}_6\text{H}_6)\text{Cl}$. When the colloid is once precipitated it may lose HCl even in a strongly acid-containing fluid.

Two hundred c.c. of the colloidal solution were diluted to 1 litre containing 5 grams HCl and heated at 130° in a Jena flask; on analysis of the total contents of the flask, $13\text{H}(\text{Fe}_2\text{O}_6\text{H}_6)_{14}\text{Cl} + 1015\text{Fe}_2\text{Cl}_6 + 28456\text{HCl}$ was obtained.

When once the HCl which was combined with the $\text{Fe}_2\text{O}_6\text{H}_6$ reunites to form a molecule of HCl, the stability of the compound disappears, and in spite of the concentration of the solution the colloid loses HCl, and the ferric hydroxide is converted into chloride. F. G. C. S.

Vanadium Sesquisulphate. ARTHUR STÄHLER and HEINZ WIRTHWEIN (*Ber.*, 1905, 38, 3978—3980. Compare Abstr., 1905, ii, 595).—*Vanadium hydrogen sulphate*, $\text{Vd}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$, obtained by methods similar to those used for the corresponding titanium salt, more especially by the electrolytic reduction of blue vanadyl sulphate, is a green, finely-crystalline, silky powder, and is

insoluble in alcohol, ether, acetic acid, or 60 per cent. sulphuric acid. Its aqueous solution has a green colour. The *ammonium* salt, $\text{Vd}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$, and *rubidium* salt have been prepared. *Vanadium sesquisulphate*, $\text{Vd}_2(\text{SO}_4)_3$, is obtained when the green salt is heated slowly at 180° in an atmosphere of carbon dioxide; it forms a microcrystalline powder, and dissolves in hydrochloric acid to a yellowish-brown, or in dilute sulphuric acid to a green solution.

J. J. S.

Modifications of Antimony. ALFRED STOCK and WERNER SIEBERT (*Ber.*, 1905, 38, 3837—3844).—A new black, amorphous modification of antimony can be prepared either by the action of oxygen or of air on liquid antimony hydride at about -40° , or by rapid cooling of the vapour of ordinary metallic antimony. Special apparatus for these operations is described, the last method consisting in distilling the metal from a porcelain tube, heated electrically by a platinum wire to about 300° , in a good vacuum on to a surface cooled by liquid air. The black antimony has a sp. gr. 5.3, it is chemically more active than the grey form, and oxidises and often catches fire in the air at the ordinary temperature. At 400° , it is converted instantly into the stable grey form and suffers the same change slowly on boiling with water; it may be freed from antimony oxide by washing with hydrochloric acid.

Antimony also exists in a third—a yellow modification. This has been so far prepared only in minute quantities either by the action of oxygen on antimony hydride at -90° , or, better, by the interaction of antimony hydride and chlorine dissolved in liquid ethane at -100° in red light. The yellow modification is very unstable; it blackens above -90° even in the dark. On shaking yellow antimony with carbon disulphide at temperatures below -50° , a suspension of insoluble antimony in the colloidal state is obtained, which above -50° is in a few seconds changed into the black modification.

Cohen's α -antimony is probably identical with the black antimony described above.

E. F. A.

Melting Point of Gold and Expansion of Gases at High Temperatures. III. ADRIEN JAQUEROD and F. LOUIS PERROT (*Arch. Sci. phys. nat.*, 1905, [iv], 20, 506—529).—The mean value for the melting point of gold in the authors' determinations was $1067.4^\circ \pm 1.8^\circ$. Previous determinations vary from 1061° to 1200° , but the three most trustworthy values are 1064.3 (Holborn and Day), 1065.6° (D. Berthelot), and the authors', giving a mean of 1065.8° , or, allowing a little more weight to the authors' value, 1066° , which they consider to be the value which should be accepted for the melting point. From the experiments, the relative values of the coefficients of expansion of the various gases employed between 0° and 1067.4° may be obtained, and, taking the value 0.0036643 for nitrogen, the other values are: air, 0.0036643; carbon monoxide, 0.0036638; oxygen, 0.0036652; carbon dioxide, (1) 0.0036756; (2) 0.0036713 (see *Abstr.*, 1905, ii, 506, 627).

L. M. J.

Precipitation of Metallic Gold. P. E. JAMESON (*J. Amer. Chem. Soc.*, 1905, 27, 1444).—By the following method, gold can be rapidly precipitated in a convenient state for collection. A stick of potassium nitrite weighing about 5 grams is placed in a solution of 1 gram of gold chloride in 30 c.c. of water, and about 3 c.c. of concentrated sulphuric acid are added immediately. When the reaction has ceased, another piece of potassium nitrite of the same size is added, and the solution is stirred until a clear pale blue solution is obtained. The precipitated gold collects at the bottom of the vessel in the form of dark brown nodules which can be easily separated by decantation.
E. G.

Hydrated Palladium Dioxide. ITALO BELLUCCI (*Zeit. anorg. Chem.*, 1905, 47, 287—288).—A reply to Wöhler and König's criticism (*Abstr.*, 1905, ii, 722) regarding the author's statements as to the composition of hydrated palladium dioxide (*Gazzetta*, 1905, 35, i, 343).
G. S.

Silesia, are white, compact masses of osteolite, embedded in which are acute scalenohedral crystals with the composition P_2O_5 , 35.90; CO_2 , 5.85; CaO , $53.30 = 95.05$; the latter are pseudomorphs of osteolite after calcite.

The published analyses of osteolite and staffelite are quoted and compared. Both these minerals differ from apatite in containing calcium carbonate in addition to phosphate; some fluorine is present in staffelite, but none in osteolite. On a specimen of staffelite from the original locality, Staffel, in Hesse-Nassau, were noticed some small, pale green, transparent crystals with the form of apatite, which were found to contain carbon dioxide. Neither in the crystals nor in the botryoidal masses of typical staffelite are there any enclosures of calcite; the carbon dioxide must therefore enter into the composition of the mineral. Staffelite and osteolite are probably identical, the latter being an impure and altered variety of the former. L. J. S.

Formation of Oceanic Salt Deposits. The Occurrence of Calcium Compounds up to 25° . JACOBUS H. VAN'T HOFF (*Zeit. anorg. Chem.*, 1905, 47, 244—280).—A summary of work already published (see Abstr., 1904, ii, 34, 417, 492, 561; 1905, ii, 319, 464, 641). G. S.

Formation of Oceanic Salt Deposits. XLIV. Limit of Existence of Tachhydrite at 83° . JACOBUS H. VAN'T HOFF and J. D'ANS (*Sitzungsber. K. Akad. Wiss. Berlin*, 1905, 913—916. Compare van't Hoff and Lichtenstein, Abstr., 1905, ii, 262, 641).—The diagram representing the conditions of separation of the various calcium compounds which play a part in the formation of oceanic deposits assumes a simpler character as the temperature rises. Solubility data are recorded for the temperature of 83° , above which tachhydrite, $CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$, is incapable of existence. These are contained in the following table, the numbers expressing mols. of salt per 1000 mols. of water:

Saturation with respect to sodium chloride and	$CaCl_2$.	$MgCl_2$.	K_2Cl_2 .	Na_2Cl_2 .
Calcium chloride ($CaCl_2 \cdot 2H_2O$)	239	0	0	0.5
Tachhydrite, magnesium chloride	141	45.5	0	0.5
Calcium chloride, potassium chloride ..	249	0	11	0.5
Calcium chloride, tachhydrite ..	239	—	0	0.5
Tachhydrite, magnesium chloride, carnallite.....	141	45.5	—	0.5
Calcium chloride, potassium chloride, carnallite ...	216	27	10.5	0.5
Calcium chloride, tachhydrite, carnallite	239	—	—	0.5

H. M. D.

Geological Thermometer. JACOBUS H. VAN'T HOFF (*Zeit. Elektrochem.*, 1905, 11, 709—710).—The temperature at which deposits of salts such as those of Stassfurt have been formed may be inferred from the properties of the salts themselves. In general, salts containing less water are formed at higher temperatures, and they are able, at the ordinary temperature, to take up water. Glauberite, $CaNa_2(SO_4)_2$, for example, combines with water and the compound melts at 29° . The melting point is depressed by other salts. The

following are the lowest temperatures at which the salts named can exist in presence of the other salts occurring with them: blödite, 5°; glauberite, 10°; hexahydrated magnesium sulphate, 13°; thenardite, 14°; kieserite, 18°; kaliblödite, 18°; octahedral borax, 34°; langbeinite, 37°; löweite, 43°; van't-Hoffite, 46°. A more accurate estimate of the temperatures at which the salts were deposited is obtained by examining the salts which can be deposited simultaneously at a given temperature. In this way it is shown that the following salts must have been deposited at temperatures above those given: glauberite, 10°; langbeinite, 37°; löweite, 43°; van't-Hoffite, 46°; löweite and glaserite, 57°; löweite and van't-Hoffite, 60°; kieserite and potassium chloride, 72°. The last appears to have been the highest temperature reached during the formation of the Stassfurt deposits. T. E.

Composition of Xenotime. WALDEMAR C. BRÖGGER (*Nyt Mag. Naturvid. Christiania*, 1904, 42, 1—7).—Kraus and Reitingner (Abstr., 1901, ii, 395) have considered xenotime (YPO_4) to be an altered form of hussakite ($3\text{R}_2\text{O}_3, 3\text{P}_2\text{O}_5, \text{SO}_3$). The perfectly fresh crystals of brown, transparent xenotime from Arö, in Norway, analysed by Blomstrand in 1890, have been examined for sulphur trioxide by O. Heidenreich, but not a trace was detected. By the replacement of part of the phosphoric oxide by small and variable amounts of sulphur trioxide, it appears that there may be a passage from true xenotime (YPO_4) to the hussakite variety (compare Abstr., 1903, ii, 553).

L. J. S.

[Columbite, Fibroferrite, Enargite, Alunogen, Doughtyite, &c.] WILLIAM P. HEADDEN (*Proc. Colorado Sci. Soc.*, 1905, 8, 55—70).—*Columbite*.—Analysis I is of columbite occurring as large masses with tourmaline in pegmatite at Canon City, Colorado. Analysis II is of similar material from Black Hills, South Dakota:

	Cb_2O_5 .	Ta_2O_5 .	WO_3 .	SnO_2 .	FeO .	MnO .	Ignition.	Total.	Sp. gr.
I.	56.48	22.12	0.45	0.11	8.07	12.45	0.15	99.83	5.66
II.	54.64	25.62	—	0.15	6.80	12.61	—	99.82	5.91

Fibroferrite.—Aggregates of greenish-white, acicular crystals from Green River, Utah, gave the results under III, agreeing with the formula $\text{Fe}_2\text{O}_3, 2\text{SO}_3, 10\text{H}_2\text{O}$:

	SO_3 .	Fe_2O_3 .	CaO, MgO .	Na_2O .	H_2O .	Insol.	Total.
III.	31.57	30.22	traces	0.59	37.06	0.10	99.54

Enargite.—The ore at the Powers Mine, Willis Gulch, Gilpin Co., Colorado, consists mainly of crystalline enargite (analysis IV), associated with some pyrites and chalcopyrite. Crystals are encrusted with quartz. Although lead is shown in the analysis, no lead mineral was detected on the specimens:

	S.	As.	Sb.	Cu.	Pb.	Fe.	Zn.	Total.	Sp. gr.
IV.	29.35	16.17	3.77	48.40	1.83	0.30	0.19	100.01	4.43

Alunogen.—This occurs as large, incrusting masses, sometimes several hundred pounds in weight, on sandstones and shales at Doughty Springs and Alum Gulch, in Delta Co., Colorado. Analysis V is of massive material (21·30 per cent. of material insoluble in water deducted); VI and VII of scaly material; VIII and IX of fibrous material. In their content of magnesia, some of these analyses show an approach to pickeringerite:

	SO ₃ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	Li ₂ O.	H ₂ O.	Insol. in H ₂ O.	Total.
V.*	37·15	15·68	trace	0·40	0·74	trace	—	—	45·81	—	100·00
VI.	37·12	13·53	trace	trace	2·90	1·25	0·17	trace	44·84	0·14	99·95
VII.	39·18	14·17	trace	0·09	1·94	not determined			43·07	0·71	99·16
VIII.	38·90	12·51	trace	trace	3·35	not determined			41·96	2·76	99·48
IX.	37·26	15·08	1·19	trace	nil	not determined			44·84	1·37	99·74
X.†	15·00	39·51	0·45	—	trace	—	—	—	41·80	1·56	100·67

* Also SiO₂ (soluble in water), 0·22. † Also SiO₂, 1·91; ZnO, 0·44.

Doughtyite.—This name is given tentatively to a hydrated basic aluminium sulphate, which is formed abundantly as a white precipitate by the interaction of the waters (an alkaline water and one containing aluminium sulphate in solution) of the Doughty Springs, Delta Co., Colorado. An air-dried sample gave results (analysis X) corresponding with the formula Al₂(SO₄)₃·5Al₂(OH)₆·21H₂O.

Bismuthite.—Analysis is given of an ore sample from the Paulina Mine, Nocoziari, Mexico, consisting of an intimate mixture of bismuthite (Bi₂S₃) and micaceous hæmatite.

Palladium.—Description is given of a soft, black material containing palladium, 11·86; copper, 60·21 per cent. It is an artificial product of unknown origin, but may possibly have been obtained from Wyoming platinum ore. L. J. S.

Minerals [Stilbite, Chabazite, &c.] from Gellivare, Sweden. A. BYGDÉN (*Bull. Geol. Inst. Univ. Upsala*, 1905, 6, (1902–3), 92–100).—In the Selets Mine, at Gellivare, the iron-ore is separated from the surrounding granulitic gneiss by a brecciated zone consisting of blocks of gneiss and ore embedded in a coarsely crystalline mixture of hornblende, magnetite, red felspar, and, sometimes, quartz. Cavities in this binding material contain zeolites. Analysis I is of stilbite, and corresponds with the formula 2RO, 2Al₂O₃, 13SiO₂, 14H₂O. Chabazite gave the results under II and III, corresponding with the formulæ RO, Al₂O₃, 4SiO₂, 6H₂O and 2RO, 2Al₂O₃, 9SiO₂, 13H₂O respectively. These zeolites are often attached to a red mineral, occurring as compact masses and as square columns, which has the composition given under IV (also trace of chlorine); it is a pseudomorph of felspar (orthoclase and plagioclase) after scapolite.

A crevice in the brecciated granulite of the Oskar Mine is filled with a soft, soapy material, which is either pale green to red (anal. V) or dark grey to violet-brown (anal. VI) in colour, the two kinds being sharply separated. When dried in the air, the material hardens and cracks, and the air-dried material crumbles when placed in water.

The substance approximates to celadonite in composition, but is probably not homogeneous :

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	CaO.	SrO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.	Sp. gr.
I.	58·22	14·68	0·22	—	0·11	7·66	—	0·51	0·44	18·22	100·06	2·14
II.	47·39	18·66	0·20	—	0·29	8·34	0·96	0·44	2·17	21·85	100·30	—
III.	49·87	17·21	0·49	—	0·46	7·74	0·61	0·30	2·27	21·15	100·10	2·09
IV.	64·18	20·11	0·75	—	0·11	1·07	—	8·97	4·04	0·78	100·01	2·63—2·67
V.	50·58	19·02	—	1·71	4·54	1·40	—	0·28	0·08	22·72	100·33	2·11
VI.	38·25	14·18	18·10	2·53	7·23	1·69	—	0·35	0·15	17·61	100·09	2·31

L. J. S.

Diffusion of Barium and Strontium in Sedimentary Rocks.
 L. COLLOT (*Compt. rend.*, 1905, 141, 832—834).—The occurrences of barytes and celestite in the sedimentary rocks of France are enumerated; they are mostly in Jurassic and Cretaceous strata, but celestite is found in the “plastic clay” and green marl of Tertiary age in the Paris basin. The minerals occur as crystals lining the cavities of fossil shells, and also as nodular concretions; in the latter case the barytes is sometimes partly replaced by calcite, giving rise to forms which have been erroneously described as organic remains.

L. J. S.

Physiological Chemistry.

The Feeding of the Frog's Heart. J. McGUIRE (*Zeit. Biol.*, 1905, 47, 289—311).—Experiments are recorded on the isolated heart of the frog which relate to facts previously known to most physiologists; for instance, that a mixture of salt solution and blood will keep the heart beating, that laked blood is toxic, that potassium chloride is poisonous, that carbon dioxide paralyses, and that temperature and season have an influence. Bowditch's staircase phenomenon is due to accumulation of carbon dioxide in the resting heart, and the improvement is due to a gradual removal of that gas with successive beats; no reference is made to Waller's theory that the phenomenon is due to the favouring action of small amounts of the same gas developed during activity. Serum, which most observers find is intensely toxic, is here spoken of as nutritive, even when deprived of all oxygen in a vacuum. W. D. H.

The Action of Carbon Dioxide on the Frog's Heart. R. H. SALTET (*Zeit. Biol.*, 1905, 47, 312—322).—This paper deals particularly with details of the harmful action of carbon dioxide on the heart. During action the output of the gas is not much increased as compared with the resting condition. The view advanced concerning the staircase phenomenon is the same as in the preceding paper. It is assumed throughout that serum albumin is the main nutritive material for

cardiac and other muscle, and carbon dioxide is stated to be harmful because it renders this proteid not capable of utilisation.

W. D. H.

Action of Nutritive Fluids on the Heart. BERTHA FINN (*Zeit. Biol.*, 1905, 47, 323—334).—A somewhat similar series of observations and conclusions. Ringer's solution is regarded as merely preservative, and not nutritive in any sense.

W. D. H.

Respiration of the Heart of Turtle and Frog. JULIA DIVINE (*Zeit. Biol.*, 1905, 47, 335—378).—Another paper of the same series, dealing especially with the reducing action the heart has on oxyhæmoglobin.

W. D. H.

Loss of Function and Recovery of the Central Nervous System in Frogs. JULIUS RIES (*Zeit. Biol.*, 1905, 47, 379—399).—The functions of the central nervous system are lost on cessation of the blood supply. No recovery occurs on subsequent perfusion with any saline solution unless mixed with proteid matter preferably obtained from serum. This and the foregoing four papers are all written with the apparent object of upholding Kronecker's theory on the importance of serum albumin for the maintenance of the nutrition of tissues, particularly those which are contractile. [No reference is made to the experiments of Locke and others which have led to a contrary conclusion.]

W. D. H.

Glycolysis. LEO RAPOPORT (*Chem. Centr.*, 1905, ii, 1371; from *Zeit. Klin. Med.*, 57, 208—214).—A consideration of the action of various tissues on sugar leads to the conclusion that glycolysis is due to ferment action.

W. D. H.

Action of Radium Rays on the Peripheral Nerves. ADOLF BECK (*Bull. Acad. Sci. Cracow*, 1905, 286—289).—The author applied a box containing 10 mg. of radium bromide to the skin covering an ending of the sciatic nerve of rabbits; in eight out of thirteen rabbits, sensibility of the foot to an induction current disappeared entirely, and in the remaining rabbits was diminished. No definite change in sensibility could be observed on a second application. The action of such small quantities of radium must be confined to the peripheral nerves, as only the foot was affected. Little or no diminution of sensibility was observed on applying radium rays to the sciatic nerve-endings of dogs.

The sensibility of the sensory nerve-endings of men was in some cases slightly increased, in others slightly decreased, on application of radium rays to the ulnar nerve.

G. Y.

Excretion of Creatinine in Man. CORNELIS A. PEKELHARING, C. J. C. HOOGENHUYZE, and H. VERPLOEGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 363—377).—The experiments recorded confirm Folin's views (*Abstr.*, 1905, ii, 183, 268) on the rôle creatinine plays in metabolism. The slight variations noticeable in the daily output

can be largely explained by the amount of creatine and creatinine in the food. The special point investigated was the influence of muscular work on the excretion. This is found to have no influence when the diet is sufficient. Creatinine is not therefore a result of energy production. Only if the food given is not sufficient does an increased output of creatinine appear; that is, in these circumstances, the material wanted for contraction is drawn from the muscular proteins.

W. D. H.

Effects of Choline on Animals. E. FARQUHAR BUZZARD and RICHARD W. ALLEN (*Rev. Neurol. Psychiatry*, 1905, 453—461).—The repeated introduction of small doses of choline into the circulating fluids of rats and rabbits does not produce any important morbid changes in the nervous system or viscera, and during life no convulsions or paralysis are seen. Large doses (greatly in excess of what can be produced in man by degenerative nervous diseases) lead to convulsive attacks. It is improbable that the convulsions of general paralysis or of epilepsy are due directly or solely to the presence of choline in the blood or cerebrospinal fluid (confirmatory of Mott and Halliburton, but against the conclusions of Donath).

W. D. H.

The Pharmacology of Indaconitine and Bikhacanitine. J. THEODORE CASH and WYNDHAM R. DUNSTAN (*Proc. Roy. Soc.*, 1905, B 76, 468—490. Compare Dunstan and Andrews, *Trans.*, 1905, 87, 1620, 1636).—Indaconitine, an alkaloid obtained from *Aconitum chamanthum*, yields on partial hydrolysis acetic acid and benzoyl-pseudoaconine; the latter substance splits up on further hydrolysis into benzoic acid and pseudoaconine. Bikhacanitine, from *A. spicatum* (*A. ferox*, var. *spicatum*), yields, under the same conditions, acetic acid, veratric acid, and a pseudoaconine identical with that obtained from indaconitine.

As regards physiological action, these two alkaloids show a qualitative agreement with aconitine, japaconitine, and pseudoaconitine, dealt with in previous papers (compare *Abstr.*, 1899, ii, 42; 1901, ii, 613). Bikhacanitine has a more powerful toxic action on cats and rabbits than indaconitine; of the alkaloids so far examined, aconitine and indaconitine are about equally poisonous, japaconitine is rather more active than these, but not quite so toxic as bikhacanitine, whilst pseudoaconitine is the most active of the series. Bikhacanitine and indaconitine are equally toxic towards frogs. The greater toxic action of bikhacanitine towards warm-blooded animals is due to its more powerful depressing effect on the respiration; the respiratory activity of frogs is also diminished to a greater extent by the former alkaloid. The relative activity of the two alkaloids in abolishing the power possessed by nerve-muscle preparations of responding to stimuli was investigated by immersing the tissues in dilute solutions of the hydrobromides, and it was found that in this respect indaconitine is slightly more active than bikhacanitine.

The pseudoaconines obtained from the two alkaloids appear to be identical in physiological action, and behave in all respects like the aconine from aconitine described in a former paper.

G. S.

Are Toxins Ferments? LEO VON LIEBERMANN (*Chem. Centr.*, 1905, ii, 1370—1371; from *Deutsch. med. Woch.*, 31, No. 33. Compare Abstr., 1904, ii, 474).—From the consideration of the quantitative relationships of such toxins as abrin and ricin, the conclusion is reached that the question in the title must be answered in the negative.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Methane as Carbon-food and Source of Energy for Bacteria. N. L. SÖHNGEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 327—331).—The fact that methane, which is produced in enormous quantities in nature and is chemically so inactive, occurs only in traces in the atmosphere led the author to search for living organisms capable of feeding on this hydrocarbon. These were discovered in short rod-like bacteria, provisionally called *Bacillus methanicus*, which form as a slimy pink film on the surface of a culture-liquid (water 100, calcium sulphate 0.01, ammonium chloride 0.10, magnesium ammonium phosphate 0.05, potassium hydrogen phosphate 0.05) impregnated with garden-soil, sewage, or canal-water, and placed in an atmosphere of methane and oxygen at about 30°. The methane is nearly all absorbed in a week and the presence of organic matter in the culture-liquid can be shown by oxidation with standard potassium permanganate. A pure culture of *B. methanicus* is obtained by growing it on washed agar, containing the necessary salts, at about 30° in an atmosphere consisting of one-third methane and two-thirds oxygen. C. S.

Similarity in the Action of Salts of Copper, Mercury, and Silver on the Lower Plants. THOMAS BOKORNY (*Chem. Zeit.*, 1905, 29, 1201—1202).—Algæ are killed by salts of copper, mercury, and silver at dilutions of 1 in 1,000,000; all other metals require to be in much more concentrated solution to exert a harmful effect. The germicidal action of ferrous sulphate is attributed to traces of copper sulphate present in this substance as an impurity. P. H.

Influence of Formaldehyde on the Energy of Increase, the Fermentation Energy, and the Duration of Generation of Different Varieties of Yeast. JULIUS HIRSCH (*Chem. Centr.*, 1905, ii, 1377—1378; from *Allgem. Zeit. Bierbrau. Malzfabr.*, 1905).—Aldehyde stimulated the energy of increase in nearly every case. The fermentation maximum was generally reached only when the energy of increase had considerably diminished. Formaldehyde does not hinder the separation of invertin. N. H. J. M.

Fermentation Process with Colophony. JEAN EFFRONT (*Chem. Centr.*, 1905, ii, 1377; from *Mon. sci.*, [iv], 19, ii, 721—722).—Abietic acid and colophony free from volatile acids are favourable

to the development of the organism. In a solution containing many yeast cells and few lactic acid bacteria, the colophony settles more on the relatively greater surface of the rods than on the yeast cells, and so assists the yeast in its struggle with the bacteria.

In practice, an alkaline solution of colophony is added after introducing the yeast into the mash; very pure fermentations result, and the sterilisation of the mash, the addition of acid, and the employment of large amounts of yeast are unnecessary.

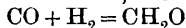
N. H. J. M.

Effect of a Drug on a Simple Vital Process. HEINRICH DRESER (*Zeit. Elektrochem.*, 1905, 11, 739—741).—The effect of sodium salicylate on the rate of evolution of carbon dioxide by yeast cells is studied. A small addition of sodium salicylate increases the rate, further quantities produce a rapid diminution in it, whilst for very large quantities the rate tends asymptotically towards a value greater than zero. The middle part of the curve can be represented by the assumption that a small addition of sodium salicylate, dx , produces a proportional increase, dy , in the rate of evolution of carbon dioxide, which is proportional to the quantity of salicylate, x , already present, or $-1/y \, dy/dx = k.x$. By putting $(x-b)$ in place of x in this equation, it is made to fit the first part of the curve also. It appears probable that a part of the salicylate is absorbed by the yeast cells and becomes inactive; the constant b would represent this absorbed part. The fact that the curve does not tend towards zero as the quantity of salicylate is increased is probably due to the superposition of another phenomenon. The evolution of carbon dioxide by Buchner's enzyme is not affected by sodium salicylate, and a small residual evolution of gas will therefore be observed after all the living yeast cells have been poisoned.

T. E.

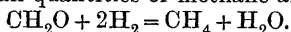
Assimilation of Carbon Dioxide. WALTHER LÖB (*Zeit. Elektrochem.*, 1905, 11, 745—752).—The author has attempted to build up a sugar from carbon dioxide and water, using the silent electric discharge in place of the natural combination of sunlight and a catalyst. The apparatus was arranged in such a way that the products formed were removed from the action of the discharge as quickly as possible.

Moist carbon dioxide yields carbon monoxide and oxygen first, formic acid and hydrogen peroxide are formed slowly as secondary products. In moist carbon monoxide, the main reactions are



(formaldehyde) and $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$. Formic acid is also produced. A moist mixture of carbon dioxide and hydrogen gives formaldehyde and formic acid. Carbon monoxide and hydrogen give the same products; the formaldehyde is, however, present in much larger quantity and considerable quantities of carbon dioxide are formed. When the discharge is passed through moist carbon dioxide in presence of a substance which absorbs oxygen, formaldehyde and formic acid are produced in much larger quantity. Chlorophyll itself may be used as the oxygen absorber.

Moist formaldehyde vapour decomposes mainly into carbon monoxide and hydrogen, but small quantities of methane are also formed :



Formic acid and water vapour behave similarly. From methane and carbon dioxide, it is almost certain that alcohol can be synthesised, and alcohol is very probably one of the intermediate products of the natural synthesis. Moist alcohol vapour alone gives a mixture of hydrocarbons, carbon monoxide, hydrogen, and a little carbon dioxide, from which further secondary products are produced. In presence of carbon dioxide, however, these reactions become of secondary importance, the main change leading to the formation of a sugar. The substance is optically inactive, it reduces Fehling's solution, and yields a crystalline osazone which melts at 160—164° and decomposes about 180°. T. E.

Assimilation by Plants during Different Periods of Growth.

HERMANN WILFARTH, HERMANN RÖMER, and GUSTAV WIMMER (*Landw. Versuchs-Stat.*, 1905, **63**, 1—70).—Whilst barley, summer wheat, peas, and mustard assimilated most of their nutritive substances by the time of flowering, the maximum was reached in the case of potatoes only at harvest time.

With the exception of phosphoric acid, more or less of the mineral constituents assimilated by barley, summer wheat, peas, and mustard return to the soil during the ripening period. With potatoes there was no return of mineral constituents to the soil.

The amount of starch increased in all the plants (except mustard) up to the ripening period. In mustard seed the starch is replaced by fat. N. H. J. M.

Influence of Nutrients on the Development of Leguminous Nodules. HENRI FLAMAND (*Bied. Centr.*, 1905, **34**, 738—740; from *Ing. agric., Gembloux*, 1904, **14**, 755).—Water-culture experiments with peas, vetches, and beans were made to ascertain the effect of different salts on the symbiosis as indicated by the production of nodules. The plants were inoculated from corresponding nodules when three weeks old.

Potassium nitrate (1:10,000) prevented the production of nodules, with sodium nitrate a larger amount (1:2000) was necessary.

Peptone has only slight effect, and urea no action at all; oxamide is injurious.

Potassium phosphate is more beneficial than the chloride and sulphate in the case of vetches and peas. With beans, the latter salts are more beneficial. Calcium and magnesium salts are very favourable in the case of peas and beans, but some of the salts hinder the production of nodules on the roots of vetches; only calcium sulphate is beneficial with vetches. N. H. J. M.

Chemotaxis of Equisetum Spermatozoids. BENGT LIDFORSS (*Chem. Centr.*, 1905, ii, 1270—1271; from *Ber. deut. bot. Ges.*, **23**, 314—316).—The specific irritant for the spermatozoids of *Equisetum* (*arvense* and *palustre*) is malic acid. The acid potassium and calcium

salts behave similarly to the normal malates and have a poisonous action. Free malic acid (1/1000 mol.) has a strongly attractive action, whilst with stronger solutions the action is reversed. Salts of maleic acid have also a strongly attractive action. Fumaric acid and its salts have no action.

N. H. J. M.

Oxidising and Reducing Properties of Living Cells. I. Oxidising Power of the Absorbent Surfaces of the Roots of Flowering Plants. M. RACIBORSKI (*Bull. Acad. Sci. Cracow*, 1905, 338—346).—The oxidising power of the absorbent surfaces of the roots of flowering plants in presence of atmospheric oxygen is demonstrated (1) by growing the plants in solutions of substances which, when sufficiently diluted, do not affect the life of the root cells, and on oxidation yield coloured products either directly or on subsequent addition of a suitable reagent, or (2) by placing the sterilised germinating seeds on moistened indicator-paper prepared from such oxidisable substances. The most suitable indicators are α -naphthylamine, benzidine, phenolphthalin, and ferrous ammonium sulphate. The following substances also are oxidised: Barbadoes aloes, guaiacum resin, phloridzin, caffetannic acid, pyrogallol, leucomethylene-blue, ursol, and tetramethyl-*p*-phenylenediamine. In no case was the oxidising power sufficient to liberate iodine from hydrogen iodide or its salts. In the absence of atmospheric oxygen, the oxidation of α -naphthylamine, benzidine, or phenolphthalin takes place slowly and to only a small extent.

The oxidising power, which is a function of the living cells, is strictly localised, being confined to the absorbent surfaces of the roots, and being strongest in the region of the root hairs. G. Y.

Root Secretions. DMITRI N. PRIANISCHNIKOFF (*Bied. Centr.*, 1905, 34, 741—743; from *Ber. deut. bot. Ges.*, 1904, 22, 184).—Millet grown in sand was found to assimilate the phosphoric acid of aluminium phosphate, both dried at 100° and ignited, and of iron phosphate when merely dried, but only small amounts when ignited. Similar results were obtained with vetches and mustard, whilst lupins utilised ignited iron phosphate.

Rye and wheat failed to develop when supplied with crude phosphates, whilst lupins produced nearly as much growth with crude phosphate as with bone phosphate.

If the different behaviour of gramineous plants and lupins towards sparingly soluble phosphates can be shown to be proportional to the production of carbon dioxide by root respiration, it would lend support to the assumption that the dissolving action of roots is due to carbon dioxide alone without intervention of free organic acids.

N. H. J. M.

The Presence of Sucrose in Scammony Root. The Presence of Sucrose in the Fresh Scammony Root. PAUL REQUIER (*J. Pharm. Chim.*, 1905, [vi], 22, 435—438, 492—494).—The dextrorotatory sugar present in the mother liquors from which crude scammonin has been precipitated (compare Abstr., 1904, i, 908)

is sucrose, which in the form of barium sucrate can be separated from the other compounds present and obtained in a crystalline form by decomposing the barium compound with carbon dioxide and recrystallising from alcohol. One hundred grams of the dry scammony root contain 3.36 grams of sucrose.

The fresh roots of scammony contain 1.872 per cent. of sucrose, which is equivalent to 6.802 per cent. of the dried root, since the fresh roots lose 72.45 per cent. on drying at 105°. M. A. W.

Malt Diastase. ANDREAS KLEEMANN (*Landw. Versuchs-Stat.*, 1905, 63, 93—134).—For each kind of barley there is a definite amount of water in presence of which the greatest amount of diastase is formed. It depends, however, how the amount of water is added and taken up. The losses of substances due to respiration are greater the greater the amount of water absorbed during the softening and germination of the grain.

The production of diastase cannot be followed with sufficient certainty by the methods hitherto available. The method employed in these experiments and found to be satisfactory is described.

N. H. J. M.

Effect of Improving Grapes on their Composition. G. CURYEL (*Bied. Centr.*, 1905, 34, 743—744; from *D. Weinlaube*, 1904, 573).—The juice of improved grapes contains more acid, more sugar, and more nitrogenous matter, but less solid constituents, especially phosphoric acid, less tannin, and less colour, than the original grapes.

N. H. J. M.

Marsh Soils. F. SCHUCHT (*J. Landw.*, 1905, 53, 309—328).—Analyses of soils from the marshes of the North Sea, and especially from the mouth of the Weser (compare *Zeits. Naturw.*, 1903, 76).

N. H. J. M.

Nitrogen Decompositions in the Soil. F. LÖHNIS (*Centr. Bakt. Par.*, 1905, ii, 15, 430—435).—The nitrogen of calcium cyanamide was very quickly converted into ammonia in April and May, and its effect on the crop resembled that of ammonium salts. As regards the decomposition of bone-meal, it was found that *Bacillus mycoides* and *Bacterium vulgare* converted 39 and 28 per cent. of the total nitrogen into ammonia in three weeks.

N. H. J. M.

Development and Distribution of Nitrates and Total Water-soluble Salts in Field Soils. F. H. KING, J. A. JEFFERY, and A. R. WHITSON (*20th Ann. Rep. Agr. Exper. Stat. Univ. Wisconsin*, for 1902—1903, 339—344).—In soils growing maize and potatoes, the nitrates in the surface soil (to one foot) increased from April to June, after which, owing to rapid growth and perhaps to heavy rains as well, there was a falling off. The amount of nitrates in the second foot was much less. In a dry season, the nitrates have a tendency to accumulate near the surface.

Determinations made from November 29 to April 1 showed in every

case except one that the soil did not contain more nitrate at the end of the frost than at the end of the autumn just before the frost.

Plants growing in rich soil were found to contain considerable amounts of nitrates, especially the lower parts of maize stems and the vines of potatoes. N. H. J. M.

Influence of the Soil on the Proteid Contents of Crops. A. R. WHITSON, F. J. WELLS, and A. VIVIAN (20th Ann. Rep. Agr. Exper. Stat. Univ. Wisconsin, 1902—1903, 345).—Pot experiments with oats, maize, and rape showed that the percentage of proteid increased with the amount of nitrate supplied. N. H. J. M.

Litter and Nitrogen [Fixation]. RICHARD HORNBERGER (*Bied. Centr.*, 1905, 34, 726—727; from *Zeit. Forst. Jagdwes.*, 1905, 37, 71. Compare Henry, Abstr., 1905, ii, 111).—After exposing leaves (oak, beech, acacia) and fir needles for a year to air and rain in zinc boxes, it was found that a gain of nitrogen, equal to only 0.3 to 0.4 kilogram per hectare, had taken place in two cases, and that in three cases there was a far greater loss of nitrogen. N. H. J. M.

Calcium Cyanamide. CONRAD VON SEELHORST and ALOYS MÜTHER (*J. Landw.*, 1905, 53, 329—356).—The results of pot experiments showed that calcium cyanamide applied to a sandy loam had a manurial value at least equal to ammonium sulphate. Good results were also obtained with a loam.

In sand-cultures, and possibly in the case of soils very deficient in fine soil, calcium cyanamide is injurious to vegetation. The poisonous action is attributed partly to the presence of calcium carbide and partly to changes in the nitrogen of the calcium cyanamide. Addition of iron oxide to sand prevents the injurious action of calcium cyanamide. N. H. J. M.

Felspar and Mica as Potassium [Manures]. DMITRI N. PRIANISCHNIKOFF (*Landw. Versuchs-Stat.*, 1905, 63, 151—156).—Experiments with different plants showed that mica is better as a source of potassium than orthoclase, and that the solvent action which ammonium salts show in the case of crude phosphates is not appreciable in the case of orthoclase. N. H. J. M.

Analytical Chemistry.

New Burette Holder. AZARIAH T. LINCOLN (*J. Amer. Chem. Soc.*, 1905, **27**, 1442—1443).—A new form of burette holder is described which has the advantages that the burettes are always vertical and parallel, can be readily put into or removed from the clamp, and can be easily moved up or down. For details, the description and diagram in the original must be consulted. E. G.

Ignition in a Vacuum by means of the Electric Furnace. ERNST HAAGN (*Chem. Zeit.*, 1905, 29, 1209).—The author recommends a special form of electrical furnace for crucibles, constructed by Heraeus, for use with a vacuum pump. With this apparatus powdered marble may be ignited to constant weight under a pressure of 40 mm. in three minutes. P. H.

Modification of Winkler's Process for the Estimation of [Dissolved] Oxygen in Water. HERMANN NOLL (*Zeit. angew. Chem.*, 1905, 18, 1767—1768).—In order to allow for the presence of organic matters in waters when using his manganese method for the estimation of dissolved oxygen, Winkler takes equal portions of the sample and of distilled water, adds to each a certain amount of manganic chloride solution, and then titrates both with thiosulphate after addition of potassium iodide. The difference in the iodine is calculated into oxygen and added to the amount found.

The author has slightly modified this procedure. Two c.c. of a 50 per cent. manganous chloride, 2 c.c. of a 40 per cent. sodium hydroxide, and 20 c.c. of water are shaken in a flask until the mass has become brown; 50 c.c. of hydrochloric acid are then added and the whole diluted to 300 c.c. To 100 c.c. of distilled water and also to 100 c.c. of the sample are now added 10 c.c. of a 5 per cent. solution of potassium iodide, and then 25 c.c. of the above manganic chloride solution, and after five minutes the iodine in both solutions is titrated. A number of experiments is given showing, however, that the correction may, as a rule, be neglected, as the action of iodine on organic matters usually occurring in waters is but trifling. L. DE K.

Volumetric Estimation of Sulphates with Benzidine Hydrochloride in Presence of Thiosulphates, Sulphites, and Sulphides. OTTO HUBER (*Chem. Zeit.*, 1905, 29, 1227—1229).—It is found that Müller and Dürke's method (*Abstr.*, 1903, ii, 751) of titrating sulphates by means of benzidine hydrochloride is not directly applicable in the presence of thiosulphates, sulphites, and sulphides; the following modified procedure is, however, recommended. By heating the mixture with a few drops of bromine the thiosulphate, sulphite, and sulphide are oxidised to sulphate; after boiling off the excess of bromine and making neutral with sodium hydroxide, the hot solution is treated with benzidine hydrochloride; this gives the total sulphate. A second portion of the solution is run into $N/10$ iodine acidified with hydrochloric acid, the excess of iodine being titrated back by means of $N/10$ thiosulphate. A third portion of the solution, after boiling with cadmium carbonate to precipitate the sodium sulphide, is cooled, made up to 250 c.c., filtered, and divided into two portions, *A* and *B*, of 100 c.c. each. *A* is again run into iodine solution and titrated back with thiosulphate, which gives the amount of thiosulphate and sulphite. *B*, after boiling for twenty-five minutes with 10 c.c. of $2N$ -acetic acid to destroy the sulphite, and 30 c.c. of $2N$ -sodium acetate, is treated with 1 gram of potassium chlorate and allowed to cool; titration with iodine then gives the amount of thiosulphate present; the addition of

sodium acetate prevents the thiosulphate from being destroyed during these operations. P. H.

Determination of the Strength of the Solutions employed in Nitrogen Determinations. FELIX MACH (*Landw. Versuchs-Stat.*, 1905, 63, 71—80).—The sodium hydroxide solution employed is rather less than $N/3$, and is prepared by diluting 225 c.c. of a solution of 1 part of sodium hydroxide in 2 parts of water to 10 litres and adding a little solid barium hydroxide. The sulphuric acid is prepared by diluting 200 grams of strong acid to 10 litres. The indicator is 2 c.c. of a solution of congo-red (2 grams) in 25 per cent. alcohol (1 litre).

The exact strength of the solution is determined by distilling a weighed amount of ammonium sulphate (about 0.4 gram) with magnesium oxide and absorbing the ammonia in 20 c.c. of the acid. Hydrogen sodium carbonate (0.6—0.7 gram) is gently heated until the weight remains constant, washed into 20 c.c. of the acid, heated to expel the carbon dioxide, and the excess of acid titrated with congo-red. Potassium tetraoxalate (0.5 gram) is dissolved in about 100 c.c. of water and directly titrated with phenolphthalein as indicator. The nitrogen value is then calculated in the usual manner.

The ammonium sulphate is prepared by adding a concentrated solution of the salt (previously recrystallised several times) to absolute alcohol (2 parts); it is then filtered, washed successively with alcohol and cooled distilled water, partially freed from water with filter paper, and stored in a moist condition.

The calcium hydrogen carbonate is prepared by passing carbon dioxide through a cold saturated solution of the carbonate. The washed precipitate is kept in a moist condition. N. H. J. M.

Estimation of Mixtures of Sulphuric and Nitric Acids. GEORG LUNGE and E. BERL (*Zeit. angew. Chem.*, 1905, 18, 1681—1687).—The investigation of the commercial mixed acids involves the determination of nitric, nitrous and sulphuric acids. It is shown that the method previously recommended for the direct estimation of the sulphuric acid, according to which the acid mixture is diluted with water, evaporated on the water-bath, and the residual acid titrated, yields results which are too low in consequence of the loss of sulphuric acid in the process. The value for the nitric acid, estimated by difference, is consequently too high. The method of examination now recommended consists in determining (a) the total acidity, (b) the nitrous acid from the permanganate titre, (c) the nitric and nitrous acids from the total nitrogen evolved in the nitrometer. The difference (c) - (b) represents the nitric acid, (a) - (c) the sulphuric acid. An alternative method is to determine the sulphuric acid gravimetrically, the nitrous acid by means of permanganate, and the nitrogen by the "nitron" method of Busch (*Abstr.*, 1905, ii, 282). The nitric acid is then given by the difference in the values of the third and second determinations. H. M. D.

Estimation of Nitric and Nitrous Acids. JACOB MEISENHEIMER and FRIEDRICH HEIM (*Ber.*, 1905, 38, 3834—3837).—The nitrite is de-

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composed by hydrogen iodide and the nitrate subsequently by ferric chloride and hydrochloric acid and the nitric oxide gas evolved in each stage of the operation measured. The operation is carried out in an atmosphere of carbon dioxide in a suitable flask and does not take longer than an hour and a half.

E. F. A.

Estimation of Nitrous Acid. FRITZ RASCHIG (*Ber.*, 1905, 38, 3911—3914. Compare Meisenheimer and Heim, preceding abstract).—In solutions with which the sulphanilic acid and permanganate methods fail, as, for example, those containing hydroxylamine, the author estimates nitrous acid by addition of potassium iodide and sulphuric acid, and, after the lapse of at least two minutes, titration of the liberated iodine with sodium thiosulphate in an atmosphere of carbon dioxide. If the thiosulphate titration is carried out too soon, results even 10 per cent. too high are obtained, probably owing to the intermediate formation of nitrosyl iodide, NOI, which decomposes slowly into nitric oxide and iodine.

The estimation of nitrous acid by means of permanganate is carried out best by adding an excess of this reagent, acidifying with sulphuric acid, and, after two minutes, determining the unused permanganate with potassium iodide and thiosulphate.

G. Y.

Estimation of Citrate-soluble and Total Phosphoric Acid in Basic Slag. FELIX MACH (*Landw. Versuchs-Stat.*, 1905, 63, 81—91).—With regard to the estimation of citrate-soluble phosphoric acid, it is shown that whilst Wagner's method generally yields satisfactory results, this is not invariably the case. It is preferable to separate the silica from the extract.

In determining total phosphoric acid, the higher results obtained by Shenke's modification is not due to the different relation between the citric acid and ammonia, but probably to impurities present in the phosphoric acid precipitate, which separates much more quickly than in the ordinary method.

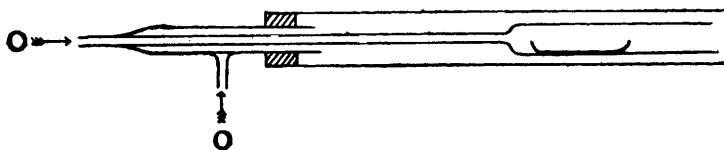
N. H. J. M.

Estimation of Arsenious Oxide. CHARLES E. CASPARI and LEO R. A. SUPPAN (*Pharm. Rev.*, 1905, 23, 334—338).—Three different methods are given for bringing arsenious oxide into solution previously to titration, all giving equally trustworthy results. First, the arsenious oxide is dissolved in warm dilute hydrochloric acid; to the solution, a slight excess of sodium hydroxide is added, the excess is neutralised with *N*-sulphuric acid, and the solution titrated with standard iodine solution after adding an excess of saturated sodium hydrogen carbonate solution. Second, the arsenious oxide is dissolved in dilute sodium hydroxide solution, the solution is cooled, neutralised with *N*-sulphuric acid, an excess of saturated sodium hydrogen carbonate solution is added, and the titration proceeded with as usual. Third, the arsenious oxide is treated with saturated sodium hydrogen carbonate solution at a boiling temperature, the solution is cooled, and any carbonate which may have formed is converted into hydrogen carbonate by the addition of a little *N*-sulphuric acid, an excess of saturated

sodium hydrogen carbonate solution is added, and the whole titrated with iodine solution.

W. P. S.

Simplified Method of Elementary Analysis for Scientific Purposes. MAXIMILIANO DENNSTEDT (*Ber.*, 1905, 38, 3729—3733. Compare Abstr., 1903, ii, 103; 1905, ii, 202, 651).—Further details of the author's method are given. The substance to be analysed is placed in a boat which is weighed in a glass tube of such dimensions that it can be readily pushed into the combustion tube. This inner tube may be closed at the one end if the substance is readily volatile, and also when the substance is difficult to volatilise, provided carbon is not deposited during the volatilisation. An open inner tube may be used for substances such as sugar and proteids which deposit much carbon on heating. Another arrangement which gives very good results permits of oxygen being passed through the outer and inner tubes at the same time (see figure).



The combustion is proceeding regularly when the contact substance glows brightly or when a small flame appears at the end of the inner tube, which is pushed close up to the contact material. This flame should remain in the inner tube, that is, it should not burn outside the rim of the inner tube. When this happens, the burner under the capillary tube is to be removed and the oxygen supply increased. This double supply method may be used for most substances and permits of the regulation of the volatilisation with great ease.

J. J. S.

Analysis of Silicates. II. EDUARD JORDIS and WILHELM LUDEWIG (*Zeit. anorg. Chem.*, 1905, 47, 180—189. Compare Abstr., 1905, ii, 317, 610).—The authors find that considerable loss by spiriting takes place when ignited silica is treated with hydrochloric acid and water, probably owing to the heat always developed when a fine powder is moistened with a liquid; this source of error is avoided by allowing the silica to cool and then moistening it with a few drops of cold water before the bulk of acid and water is added. The amount of silicic acid which passes into solution during the washing of the ignited silica on the filter depends largely on the base with which the silica has been combined; it is very small with barium and strontium silicates, much greater with calcium silicate, and is greatly increased by the presence of alkali metals. The colloidal silicic acid remains in solution in the filtrate, even in the presence of a large excess of an alkali chloride.

Kehrman and Flürscheim's suggestion (Abstr., 1905, ii, 411) as to the volatility of silicic acid is inaccurate; the discrepancies observed are due to the foregoing sources of error, and it is shown that when proper precautions are taken there is no appreciable loss.

G. S.

Simplified Method for Determining Potassium, Sodium, Calcium, Magnesium, and Phosphoric Acid in Hydrochloric Acid Soil Extracts. HUGO NEUBAUER (*Landw. Versuchs-Stat.*, 1905, 63, 141—149).—A portion of the extract corresponding with 25 grams of soil is evaporated to dryness, after adding calcium carbonate (0.5 gram) in the case of soils which do not effervesce with acid, heated over a mushroom burner, rubbed with a glass pestle, and again heated until the organic matter is destroyed. It is then boiled with about 60 c.c. of water for half an hour, diluted to 125 c.c., and filtered. The filtrate should be quite colourless and slightly alkaline. Potassium is determined in 100 c.c., as previously described (*Abstr.*, 1900, ii, 481), and also the sodium (*Abstr.*, 1904, ii, 209). The phosphoric acid is determined in the insoluble residue, which is boiled for half an hour with dilute sulphuric acid (containing 5 c.c. of strong acid). The solution is diluted to 100 c.c. and precipitated with molybdate solution (100 c.c.) prepared without ammonium nitrate (*Abstr.*, 1903, ii, 102). Or the phosphoric acid may be determined, preferably by von Lorenz' method (*Abstr.*, 1901, ii, 278), in 25 c.c. of the solution (= 5 grams of soil) after adding 25 c.c. of nitric acid of sp. gr. 1.2.

Calcium and magnesium are estimated in another portion of the original solution (corresponding with 25 grams of soil). After evaporating to dryness and heating as before, the residue is heated with water and 2—5 grams of ammonium chloride (according to the amount of calcium) until no more ammonia is given off, washed into a 125 c.c. flask, and boiled with a few drops of ammonia. The cold solution is diluted to 125 c.c., filtered, and the calcium and magnesium estimated in 100 c.c. by the usual methods.

The method is suitable for all soils except those which contain very large amounts of sulphates.

N. H. J. M.

The Use of the Rotating Anode for the Estimation of Cadmium taken as the Chloride. CHARLES P. FLORA (*Amer. J. Sci.*, 1905, [iv], 20, 392—396).—When substituting cadmium chloride for the sulphate (*Abstr.*, 1905, ii, 859), some important differences were noted. Good results were obtained in solutions containing sulphuric acid, cyanides, and pyrophosphates, but with phosphates such care is required that the phosphate method cannot be recommended when other methods are available. With great care, fair results may be got in the presence of urea, formaldehyde, and acetaldehyde. In presence of acetates, the method proved unworkable with cadmium chloride, although the results had been most satisfactory in the case of the sulphate.

L. DE K.

Microchemical Reaction for Copper in Presence of Lead and Bismuth. PIETER A. MEERBURG and H. FILIPPO (*Chem. Centr.*, 1905, ii, 1466; from *Chem. Weekblad.*, 2, 641—643).—The presence of 0.0001 mg. of copper can be detected by adding caesium chloride to the solution of the copper salt in hydrochloric acid. When a small quantity of caesium chloride is added to a solution of a copper salt, red, needle-shaped or six-sided prismatic crystals ($\text{CuCl}_2 \cdot \text{CsCl}$?) are formed together with other colourless compounds; the addition of a further

quantity of caesium chloride causes the separation of yellow crystals ($\text{CuCl}_2 \cdot 2\text{CsCl}$?), from which the red crystals may be regenerated by again increasing the quantity of cupric chloride. The long, prismatic crystals cause a marked polarisation of light, but the shorter ones have, as a rule, no such action. The presence of hydrochloric acid appears to accelerate the reaction for copper, but cobalt and iron may interfere even in the presence of ammonium chloride. The iron may be removed as ferric oxide by repeatedly evaporating the solution, but the cobalt cannot be separated. When a small quantity of caesium chloride is added to a solution containing cobalt, reddish-brown crystals are formed and yellow or yellowish-green crystals separate on the addition of a larger quantity of caesium chloride. Lead and bismuth have no effect on the reaction, and in mixtures of these metals with copper, bismuth may be detected simultaneously by Behren's reaction, and the lead finally obtained as caesium lead copper nitrite. When a large quantity of lead is present, colourless, highly refractive, apparently rhombohedral crystals are sometimes formed. E. W. W.

Gasometric Estimation of Copper with Hydrazine Salts. ERICH EBLER (*Zeit. anorg. Chem.*, 1905, 47, 371—376).—The author finds that the oxidation of hydrazine salts by solutions of cuprammonium salts proceeds strictly in accordance with the equation

$$4(\text{CuSO}_4, 4\text{NH}_3) + \text{N}_2\text{H}_4, \text{H}_2\text{SO}_4 =$$

$$2(\text{Cu}_2\text{SO}_4, 4\text{NH}_3) + \text{N}_2 + 2\text{NH}_3 + 2(\text{NH}_4)_2\text{SO}_4$$

under all conditions, and on this fact has been based a method for the estimation of copper and of hydrazine compounds by measurement of the evolved nitrogen. The reacting substances are heated together, without access of air, in an apparatus described by Hempel, and the nitrogen measured over mercury. Test analyses gave satisfactory results.

Metallic salts which themselves reduce hydrazine exert a disturbing action and must be removed before the experiment; this can be effected satisfactorily by precipitation as metal with a hydroxylamine or hydrazine salt, the copper remaining in solution as the cuprammonium compound. G. S.

Gasometric and Volumetric Estimation of Mercury by Hydrazine Salts and Gasometric Estimation of Hydrazine by Mercury Salts. ERICH EBLER (*Zeit. anorg. Chem.*, 1905, 47, 377—385).—When mercuric salts, dissolved in acetic acid containing sodium acetate, are gently heated with hydrazine salts, they are reduced quantitatively according to the equation $2\text{HgCl}_2 + \text{N}_2\text{H}_4 = 4\text{HCl} + 2\text{Hg} + \text{N}_2$. This reaction may be made use of for the estimation both of hydrazine and of mercuric salts by measurement of the evolved nitrogen. For this purpose the reacting substances are heated in an atmosphere of carbon dioxide, the nitrogen is driven over into a Schiff's nitrometer containing potassium hydroxide, and subsequently measured over mercury.

Mercuric salts in ammoniacal solution are also reduced completely by hydrazine salts, and the reaction may be employed for the quantitative estimation of mercuric salts, either by measuring the

volume of nitrogen evolved, as previously described for copper (see preceding abstract), or by titrating the excess of hydrazine salt. According to the latter method, ammonia is added to a weighed quantity of the mercuric salt, dissolved in hydrochloric acid, until the solution becomes clear, a known excess of 1/40 normal hydrazine sulphate is added, the mixture is then heated on the water-bath until the precipitate has settled, allowed to cool, made up to a definite volume, filtered, and an aliquot part titrated with iodine by the method given by Stolle (*Abstr.*, 1903, ii, 100).

These methods for the estimation of mercury are also applicable to mixtures, except when substances such as silver and copper, which are themselves reduced by hydrazine, are present; a method of removing these metals by means of hydrazine is described. G. S.

Influence of the Presence of Titanium on the Estimation of Aluminium in Presence of Iron and Phosphoric Acid. HENRI PELLET and CH. FRIBOURG (*Ann. Chim. anal.*, 1905, 10, 416—420).—Experiments still in progress, showing that the processes now in use for estimating aluminium in presence of iron or phosphoric acid all give an alumina contaminated with titanium oxide should this be present in the ashes of plants, &c., operated upon.

The weighed alumina compound should therefore be fused with potassium hydrogen sulphate, and the resulting solution tested colorimetrically with hydrogen peroxide. It is still doubtful whether the titanium occurs in the precipitate as oxide or phosphate.

L. DE K.

Estimation of Metallic Iron in Reduced Iron. H. CORMIMBEUFF and L. GROSMAËN (*Ann. Chim. anal.*, 1905, 10, 420—422).—One gram of the sample is treated for six hours with 25 c.c. of 2*N* iodine with occasional shaking. Two hundred and fifty c.c. of water are then added and the uncombined iodine titrated with 2*N* sodium thiosulphate. One c.c. of iodine solution = 0.056 gram of metallic iron. L. DE K.

Separation of Iron from Zinc by means of Ammonia. W. FUNK (*Zeit. angew. Chem.*, 1905, 18, 1687—1689).—The ferric iron solution is mixed with excess of ammonium chloride and then neutralised with ammonia. Sufficient ammonia is now added to fully precipitate the iron, and then an excess of about thirty times the amount already used. The whole is heated to 70—80°, and the precipitate is collected and washed with a hot 5 per cent. solution of ammonium chloride. To remove the zinc completely, the precipitate must be redissolved in hot dilute hydrochloric acid and reprecipitated in the same manner.

The zinc may be titrated in the filtrate by the usual process. The iron precipitate may then be washed, ignited, and weighed. Allowance must be made for any silica present. As this renders the estimation troublesome, the author prefers the acetate method for the estimation of iron in presence of zinc.

L. DE K.

Estimation of Tin in Copper-Tin Alloys. ARTHUR G. LEVY (*Analyst*, 1905, 30, 361—364).—The alloy is distilled in a current of chlorine and the volatile stannic chloride collected in receivers containing water. About 0.5 gram of the finely-divided alloy is placed in a 30 c.c. distillation flask, the side-tube of which is bent first up for a short distance and then down again, so that any drops of liquid projected into the side-tube drain back into the flask. The flask is connected with two Volhard receivers containing water, india-rubber stoppers and connections being used. The entry tube for the chlorine reaches about half-way down the bulb part of the flask; around it, and below the side-tube, is wrapped a fairly tight plug of glass wool to retain the fine spray of other chlorides carried up by the stannic chloride. The chlorine is passed through a wash-bottle containing concentrated hydrochloric acid, and is then thoroughly dried before it enters the distillation flask. The latter is gently warmed when it has become filled with chlorine. The last traces of stannic chloride are removed from the flask by adding about 10 c.c. of hydrochloric acid and continuing the distillation until the bulk of the acid has been distilled off. The stannic chloride in the receivers is precipitated with hydrogen sulphide and weighed as the oxide. If antimony is present in the alloy, it will distil with the tin, and may be separated by the usual methods.

W. P. S.

Estimation of Bismuth. Separation from Copper, Cadmium, Mercury, and Silver. ARTHUR STAEBLER and WILHELM SCHARFENBERG (*Ber.*, 1905, 38, 3862—3869).—The precipitation of bismuth as phosphate in presence of dilute nitric acid does not yield satisfactory results, as the bismuth is liable to dissolve slightly, especially if hydrochloric acid is present. This difficulty can be overcome by precipitating in presence of phosphoric acid, which dissolves the phosphates of copper, cadmium, silver, and mercury; lead phosphate is too sparingly soluble to be easily separated in this way. The actual precipitation is carried out by adding hot sodium phosphate to a boiling solution of the bismuth salt acidified with nitric acid, in order to prevent the separation of basic salt. Analyses are given to illustrate the separation of bismuth from chlorides, from copper, from cadmium, from mercury, and from silver. Cadmium is separated most exactly by electrolysis, the electrolyte being prepared by dissolving the sulphide in nitric acid. Mercury can be separated quickly and exactly from a hot ammoniacal solution as sulphide entirely free from excess of sulphur.

T. M. L.

Estimation of Bismuth and Separation from the Heavy Metals as Phosphate. HEINRICH SALKOWSKI [with BERNHARD SENDHOFF] (*Ber.*, 1905, 38, 3943—3944. Compare *J. pr. Chem.*, 1868, [i], 104, 172).—Bismuth is precipitated and separated quantitatively from copper, cadmium, mercury, silver, lead, iron, manganese, cobalt, nickel, zinc, chromium, and aluminium as the phosphate in nitric acid solution, which must be free from hydrochloric acid or chlorides. The precipitate, which can be ignited without risk of reduction, is weighed as

BiPO_4 . The insolubility of bismuth phosphate in dilute nitric acid solution may be utilised for the detection of the metal. G. Y.

Temperature of Combustion of Methane in the Presence of Palladiumised Asbestos. H. G. DENHAM (*J. Soc. Chem. Ind.*, 1905, 24, (xxiii), 1202—1205).—Different observers give widely-varying estimates of the maximum temperature at which the hydrogen in a gaseous mixture can be burnt over palladiumised asbestos without the simultaneous combustion of methane (compare Phillips, Abstr., 1894, ii, 293; Richardt, Abstr., 1904, ii, 167). The author finds that a mixture of methane and oxygen, in the proportions for complete combustion, passing over palladiumised asbestos at the rate of 1 c.c. per $3\frac{1}{2}$ sec., begins to burn at $514\text{--}546^\circ$; at twice the speed, the temperature is about 50° higher. The temperature of initial combustion rises when the proportion of either gas is increased, and is not lowered by the addition of hydrogen.

Carefully prepared palladiumised asbestos gives consistent results in such combustion provided the temperature does not rise above $500\text{--}550^\circ$.

That the action of the catalyst is not due to superficial oxidation was proved by passing oxygen over the palladiumised asbestos, displacing the oxygen by nitrogen and the latter by methane; carbon dioxide was not produced at 600° . C. S.

The Iodine Value of Mineral Oils. EDMUND GRAEFE (*Chem. Rev. Fett. Harz. Ind.*, 1905, 12, 296—299).—The quantity of unsaturated compounds in commercial mineral oils may be approximately estimated from the iodine value of the oil, but allowance must be made for the sulphur compounds also existing in crude oils (Abstr., 1904, ii, 514). In conjunction with the bromine and sulphuric acid tests, the iodine value is of use in detecting coal tar products in mineral oils. Petroleum oil remains uncoloured when carefully poured on the surface of warm sulphuric acid, whilst other oils are coloured yellow or brown. American petroleum absorbs considerably more bromine than do oils from other countries. W. P. S.

Detection of Methyl Alcohol in Liquids containing Ethyl Alcohol. FRANZ UTZ (*Chem. Centr.*, 1905, ii, 1467; from *Pharm. Centr.-H.*, 46, 736—737).—In order to detect the presence of methyl alcohol in liquids which contain ethyl alcohol, Kalm (*D.-Am. Apoth. Zeit.*) recommends the following method. 0.5—1.0 c.c. of the liquid to be tested is diluted to 5—10 c.c. with water, and a red-hot copper spiral is repeatedly plunged into the solution. When 5 c.c. of milk and a solution of ferric chloride are then added and the mixture poured on to concentrated sulphuric acid, a violet-blue line is formed at the zone of contact of the two layers if methyl alcohol is present in the original sample. The author finds that even when the quantity of methyl alcohol is small, the formaldehyde which is formed by the oxidising action of the cupric oxide is not lost by volatilisation. Acetone gives a similar reaction, but the colour is not so intense as that formed in the case of methyl alcohol. E. W. W.

Detection of Methylated Spirit in Tinctures, &c. ERNST SCHMIDT and RUDOLF GAZE (*Arch. Pharm.*, 1905, 243, 555—558).—Detailed directions are given for the testing of various spirits and tinctures in order to find whether they have been made with alcohol to every 100 litres of which 5 of methyl alcohol containing 30 per cent. of acetone have been added. Preparations made with methylated alcohol of this description have been put on the market lately.

C. F. B.

Estimation of Sugars. JULES WOLFF (*Ann. Chim. anal.*, 1905, 10, 427—431).—The amount of the precipitated cuprous oxide is estimated by dissolving it in an acid solution of ferric sulphate (free from ferrous iron) and then titrating the ferrous iron formed with permanganate.

L. DE K.

Calculation of the Proportion of Lactose Hydrolysed in a Solution of this Sugar submitted to the Action of Lactase. Measurement of the Activity of Lactase. CH. PORCHER (*Bull. Soc. chim.*, 1905, [iii], 33, 1285—1295. Compare Porcher, *Abstr.*, 1905, ii, 540, and Brachin, *Abstr.*, 1904, i, 1069).—A critical résumé of the polarimetric, phenylosazone, iodometric, and cupric reduction methods of estimating galactose and dextrose in presence of lactose is given, and it is shown that the method based on the reduction of Fehling's solution gives the best results when only small quantities of the two hexoses are present. For this reason, this method is best adapted for the measurement of the hydrolytic activity of lactase towards lactose. A detailed description of the method adopted by the author in carrying out such estimations and a graphic method of calculating the results are given in the original.

T. A. H.

Polarimetric Estimation of Starch. ERICH EWERS (*Zeit. öffentl. Chem.*, 1905, 11, 407—415).—Starch is completely dissolved by successive treatment with glacial acetic acid, dilute hydrochloric acid, and hot water, and the solution obtained may be examined in the polariscope. The following conditions are necessary for the attainment of correct results: 10 grams of the starch, or starchy substance, are heated in a flask with 50 c.c. of glacial acetic acid, the flask being immersed in a boiling water-bath for twenty minutes. About 130 c.c. of cold water are then added and the heating continued for one hour at a temperature of 45°. In the case of potato starch, the digestion with water at 45° must be omitted. After cooling, from 2 to 3 c.c. of saturated potassium ferrocyanide solution are added, the liquid is diluted to 200 c.c., filtered, and the filtrate polarised in a 200 mm. tube at a temperature of 20°. The reading, which will be quite small (generally + 0.2 degree of the Ventzke scale), gives the amount of soluble carbohydrate in the sample. A second quantity of 10 grams of the starch is then heated with 50 c.c. of glacial acetic acid for ten minutes in a boiling water-bath. Ten c.c. of dilute hydrochloric acid (1:10) are now added and the digestion continued for exactly six minutes. The mixture is then diluted with water to a volume of 180 c.c., and heated for a further fifteen minutes, except in the case of potato starch. The solution is finally "cleared" with potassium

ferrocyanide, diluted to a volume of 200 c.c., filtered, and polarised. From the experiments described it is seen that all starches give approximately the same reading when the latter is calculated on the pure dry starch. For instance, the following readings were obtained with various starches when treated as above: wheat starch, $+52.7^{\circ}$; wheat flour, $+52.7^{\circ}$; rice starch, $+52.6^{\circ}$; maize starch, $+52.4^{\circ}$; potato starch, $+53.8^{\circ}$ Ventzke, when the actual readings were calculated on the quantity of pure starch known to be present in the samples.

W. P. S.

Direct Estimation of Acetyl and Benzoyl Groups. RICHARD MEYER and ERNST HARTMANN (*Ber.*, 1905, 38, 3956—3958. Compare R. and H. Meyer, *Abstr.*, 1896, ii, 226; A. G. Perkin, *Trans.*, 1905, 87, 107; Sudborough and Thomas, *ibid.*, 1752).—0.5—0.7 gram of the substance is heated in a reflux apparatus for one hour with 5 grams of pure sodium hydroxide and 50 c.c. of methyl alcohol which has been distilled over potassium carbonate. The solution is then cooled, acidified with 50 c.c. of phosphoric acid of sp. gr. 1.104, then distilled with steam and the distillate titrated with 0.1*N* barium hydroxide, using phenolphthalein as indicator. Benzoyl groups are estimated in the same way.

Attention is drawn to the fact that acid is formed when either methyl or ethyl alcohol is boiled for some time with sodium hydroxide.

J. J. S.

Hydrolysis of Sodium Palmitate. ROBERT COHN (*Ber.*, 1905, 38, 3781—3784. Compare *Zeit. öffentl. Chem.*, 1905, 11, 58; Kanitz, *Abstr.*, 1903, ii, 248).—In reply to Schwarz (this vol., ii, 657), the author gives experimental details to show that sodium hydroxide can be estimated accurately in aqueous solution in presence of sodium palmitate by titration of the hot solution with aqueous *N*/2 hydrochloric acid, with phenolphthalein as indicator, and taking as the neutral point the change of colour from deep red to a light rose.

The total sodium, present as hydroxide and as palmitate, is determined by titration of the hot aqueous solution with *N*/2 hydrochloric acid, using methyl-orange as indicator.

G. Y.

Detection of Foreign Colouring Matters in Fats. GEORG FENDLER (*Chem. Rev. Fett. Harz. Ind.*, 1905, 12, 207—209 and 237—239).—Of all the methods proposed for the detection of added colouring matters in fats, and particularly in butter and margarine, not one serves as a general test for each or all of the colours usually employed. The hydrochloric acid test only gives positive indications in the case of a few azo-dyes. On treating butter with a freshly-prepared ethereal solution of nitrous acid, the fat is completely decolorised, even if saffron, marigold, Orleans-yellow, or Martius-yellow is present, whilst turmeric, aniline-yellow, tropæolin, dimethyl-aminoazobenzene, and certain "butter colours" are not affected. Extracting the fat by shaking with alcohol affords useful information as to the presence of foreign colours, especially if the alcohol becomes strongly tinted, but as nearly all fats are soluble to a slight extent in

alcohol, the coloration obtained must be compared with that yielded by a similar fat known to be uncoloured.

W. P. S.

Behaviour of Milk towards Magenta-Sulphurous Acid Solution and the Detection of Formaldehyde in Milk. EICHHOLZ (*Milchw. Zentr.*, 1905, 1, 499—500).—The proteids of milk have the property of giving a red coloration when treated with a solution of magenta decolorised with sodium sulphite, but this property is destroyed by the addition of a trace of acid or alkali. On the other hand, a solution of magenta bleached by means of sulphurous acid (Schiff's reagent) only gives a coloration with milk when the latter contains formaldehyde. As formaldehyde after a time combines with the albumin of the milk and no longer gives a coloration with Schiff's reagent, it is better to distil the milk and apply the test to the distillate.

W. P. S.

Detection of Formaldehyde in Witch Hazel. WILLIAM A. PUCKNER (*Amer. J. Pharm.*, 1905, 77, 501—503).—The following test is proposed as an improvement on the United States official test for the detection of formaldehyde in "witch-hazel extract," a preparation resembling the Liquor Hamamelidis of the B.P. One c.c. of the solution is added to 5 c.c. of a freshly-prepared solution of 0.01 gram of salicylic acid in 100 c.c. of concentrated sulphuric acid. If as little as 1 gram of formaldehyde in 10,000 c.c. is present, a red coloration is produced. The quantity of salicylic acid used must not exceed the amount stated, or the sensitiveness of the test will be impaired.

W. P. S.

Sensitive Colour Reaction for Formaldehyde, Oxygenated Compounds of Nitrogen, or Proteid Matters. E. VOISENET (*Bull. Soc. chim.*, 1905, [iii], 33, 1198—1214).—When 0.1 gram of albumin is dissolved in 2 or 3 c.c. of water and to this is added a drop of a solution containing 5 per cent. of formaldehyde, then, on the addition of from 6 to 9 c.c. of hydrochloric acid ($\frac{3}{4}N$) containing 0.01 gram of nitrous acid per litre, the liquid acquires immediately a rose tint, which becomes rose-violet and finally passes into an intense bluish-violet.

Investigation of the conditions under which this reaction takes place shows that the colour forms most readily at a temperature of 50°, that it is not produced if any one of the three substances, proteid, formaldehyde, or nitrous acid, is in excess, and that hydrochloric acid may be replaced by sulphuric acid.

Feeble pink colorations are produced by the action on proteid matters of hydrochloric acid containing nitrous acid in the absence of formaldehyde, but these are quite distinct from the intense colours produced in presence of the aldehyde. The formation of the colour seems to be due to the interaction of the formaldehyde with the oxidation products formed by the action of nitrous acid on the scatole, indole, or similar substances produced by the action of hydrochloric or sulphuric acid on the proteids: thus the coloration is given by most proteids, by the products of pancreatic digestion of proteid, and by scatole and indole, but not by the products of peptic digestion.

Similarly, nitrous acid may be replaced by almost any oxidising agent. Formaldehyde is the only aliphatic aldehyde which gives the coloration, though similar colorations are given by some of the aromatic aldehydes. A distinct coloration is produced by solutions containing one part of formaldehyde in 10,000,000 of water. It is suggested that the reaction may be utilised for the detection of formaldehyde in food-stuffs, nitrous products in sulphuric or hydrochloric acid, nitrates in water, added water (containing nitrates) in milk, or albumin in urine. Precise directions for the use of the reaction in these special cases are given in the original. T. A. H.

Estimation of Caffeine in the Presence of Acetanilide. WILLIAM A. PUCKNER (*Pharm. Rev.*, 1905, 23, 345—350).—Both caffeine and acetanilide may be estimated in headache remedies by the following method. About 1.5 grams of the sample are treated with 30 c.c. of water containing 2 c.c. of *N* sulphuric acid. The solution is extracted five times with chloroform, using 20 c.c. each time, and the extracts filtered through asbestos into a flask. The chloroform is then distilled off and the residue dried at 100° and weighed. The residue is now dissolved in 50 c.c. of boiling water, cooled, and the excess of acetanilide allowed to crystallise out. The crystals are collected on a small cotton-wool filter and washed with about 25 c.c. of water. The filtrate and washings are treated with 1 c.c. of dilute hydrochloric acid and 25 c.c. of *N*/5 iodine solution, and shaken occasionally for half an hour. The precipitate of caffeine periodide is collected on an asbestos filter, washed with 25 c.c. of *N*/10 iodine solution containing about 0.25 c.c. of hydrochloric acid, and then dissolved in a solution of 2 grams of sodium sulphite in 10 c.c. of water. The filter is washed with about 15 c.c. of water and the solution and washings extracted several times with chloroform. The residue obtained on evaporating the chloroform is dried for three hours at 100° and weighed. The method yields about 99 per cent. of the caffeine actually present in the sample. W. P. S.

Choline Periodide and the Quantitative Precipitation of Choline by Potassium Tri-iodide. VLADIMÍR STANĚK (*Zeit. physiol. Chem.*, 1905, 46, 280—285).—Choline periodide, which is obtained by the addition of iodo-potassium iodide to a solution of choline, was first described by Griess and Harrow (*Trans.*, 1885, 47, 298); it can be obtained in crystalline form, and may be used for the estimation of choline. It is suggested that this reaction may be employed to determine the amount of choline in animal and vegetable tissues. The periodide has the composition $C_5H_{14}ONI_3$, and it may therefore be spoken of as an enneaiodide. W. D. H.

General and Physical Chemistry.

Supposed Relationship between Molecular Size and Rotatory Power in Solutions. THOMAS S. PATTERSON (*Ber.*, 1905, 38, 4090—4101. Compare Walden, *Abstr.*, 1905, ii, 130).—Walden states that there is a relationship between the molecular weight of a compound in solution and its rotatory power. The figures quoted for ethyl tartrate are invalidated by differences in the temperature at which experiments were made in different solvents, and doubt is also cast on the validity of the molecular weight determinations on account of excessive concentration of the solutions. The most striking adverse evidence is found in the case of solutions of ethyl tartrate in benzene, where, in spite of a very great change of molecular weight, the rotatory power is the same at 5 and at 25 per cent. concentrations; in aqueous solutions, on the other hand, the molecular weight remains constant, but the rotatory power varies widely. Several other examples are quoted which go to show that the relationship postulated by Walden does not exist.

T. M. L.

Solubility and Specific Rotatory Power of Carbohydrates and certain Organic Acids and Bases in Pyridine and other Solvents. JOSEPH GERARD HOLTY (*J. Physical Chem.*, 1905, 9, 764—779).—The author's experiments were performed chiefly with pyridine solutions, for which the following solubilities are given: lævulose, 18.49; malic acid, 14.6; dextrose, 7.62; sucrose, 6.45; galactose, 5.45; erythritol, 2.50; lactose, 2.18; strychnine, 1.23; mannitol, 0.47. Propyl tartrate was found to be miscible with pyridine. The specific rotation of lactose was less in pyridine than in aqueous solution and decreased with dilution. For dextrose and galactose, the rotation was greater than for the equally concentrated aqueous solution. For lævulose, the lævorotation was much less than that of the aqueous solution, the values for a 7.6 per cent. solution being: pyridine, -36.8 ; water, -87.3 . The lævorotations of mannitol and malic acid are considerably greater than those of the aqueous solution, values for a 7.6 per cent. solution being respectively -26.9 and -2.07 in the case of malic acid. Strychnine gave a lævorotatory solution of higher specific rotation than the corresponding solution in chloroform. For a 6.45 per cent. solution of sucrose, the specific rotation was 82.97 , and the value increases slightly with dilution. From his inability to verify it experimentally, the author considers that the theory of a greater solubility for small than for large particles is not true in the case of pyridine solutions of sucrose.

L. M. J.

Action of Alkaline Uranyl Salts on the Rotatory Power of Sugars and other Optically-active Hydroxyl Compounds. HERMANN GROSSMANN (*Zeit. Ver. deut. Zucker.-Ind.*, 1905, 1058—1073).—Lævulose and mannitol react readily with alkaline uranyl solutions,

forming intensely golden-yellow alkaline liquids, the rotations of which differ considerably from the true rotations of the optically-active compounds. Complex compounds, in which the alcoholic hydrogen atoms are replaced by the uranyl-residue, are here formed. The addition of 1 mol. of uranyl salt to 1 mol. of lævulose or mannitol changes the direction of the rotation. Dextrose, galactose, lactose, and rhamnose also exhibit similar changes in rotation, but the direction of the latter is not reversed. Sucrose is slowly transformed into lævoro-rotatory alkali-uranyl compounds, but no change of the sugar molecule appears to take place here. The optical activity of mannitol is accentuated by a number of compounds, for instance, boric, molybdic, and uranic acids.

The increase in the rotation of tartaric acid by uranyl nitrate and sodium hydroxide observed by Walden (*Ber.*, 1897, 30, 2889) is not a reaction occurring in alkaline solution, but requires the presence of hydrogen ions, so that the hydrogen atoms of the hydroxyl groups are probably not replaced by uranyl-residues. Saccharic acid exhibits, on the whole, similar behaviour, its direction of rotation being reversed.

T. H. P.

Spectrum Analysis of the Light emitted by Crystals of Radium Bromide. F. HIMSTEDT and G. MEYER (*Chem. Centr.*, 1905, ii, 1661; from *Physikal. Zeit.*, 6, 688—689. Compare Sir William and Lady Huggins, *Abstr.*, 1904, ii, 4).—In order to examine the spectra of the light emitted by radium bromide, three crystals were arranged in front of the collimator tube of a quartz spectrograph in such a way that they did not touch each other. The whole apparatus was enclosed in an opaque air-tight case, which was filled with dry air, hydrogen, or carbon dioxide. After an exposure of seven to ten days, the photograph showed three continuous spectra extending from $460\mu\mu$ to $337\mu\mu$. The blackest portion reached to $380\mu\mu$, and when the case was filled with air the nitrogen bands in this region were only faintly visible. Beyond $380\mu\mu$, however, the nitrogen bands could be identified with certainty and were distinctly apparent in the spaces which separated the spectra. The nitrogen line, $315.9\mu\mu$, extended with equal intensity from the bottom to the top of the plate. The nitrogen in the atmosphere near the crystals must therefore have been rendered luminous. The presence of traces of moisture was found to decrease the intensity of the light considerably. When an atmosphere of dry hydrogen or carbon dioxide was used, the three continuous spectra extended to $310\mu\mu$, and did not show any traces of bands or lines in the intervening spaces. The strongest fluorescence was observed in an atmosphere of carbon dioxide. The wave-lengths of the nitrogen light are the same in the case of radium bromide and of radiotellurium.

E. W. W.

Some Phosphorescence Spectra indicating the Existence of New Elements. Sir WILLIAM CROOKES (*Chem. News*, 1905, 92, 273—274).—Sub-fractionation has yielded earths in which certain groups of unassigned lines and bands of the phosphorescent spectra grow fainter or stronger independently of both other unassigned

groups and of groups of lines assigned to known elements. These are provisionally regarded as indicating new elements. D. A. L.

Radium in Sweden. JOHN LANDIN (*Arkiv Kem., Min. Geol.*, 1905, 2, i, No. 2, 1—7).—The author has demonstrated the presence of radium in culm by preparing from it barium sulphate and testing the action of the latter on a photographic plate. The alum schists of Billinge answer to the same test, and, like culm, also contain uranium. The quantity of radium in these minerals is, however, too small to be of industrial importance. Hjelmite crystals slowly blacken a photographic plate. T. H. P.

Emission of Heat by Radium. KNUT ÅNGSTRÖM (*Chem. Centr.*, 1905, ii, 1575; from *Physikal. Zeit.*, 6, 685—688).—Since the quantity of heat emitted by radium does not decrease to an appreciable extent in a year and is not dependent on the nature of the surrounding medium, the energy lost in the form of α -, β -, and γ -rays can only be a very small proportion of the total energy (compare Paschen, *Abstr.*, 1904, ii, 798). Measurements have been made by an electrical compensation method in which an equal quantity of heat was generated electrically and balanced against a sensitive thermo-element. 86.5 mg. of radium bromide were used. Lead, copper, and aluminium calorimeters were used, the results differing by not more than 2 per cent. When about 1/7 of the γ -rays which passed through the aluminium calorimeter were absorbed by a cylinder of lead, the quantity of heat imparted to the cylinder was not equal to 1 per cent. of the quantity liberated in the calorimeter; the energy of the β - and γ -rays cannot, therefore, be equal to more than a few parts per 100 of the total energy emitted by the radium. The mean value of the quantity of heat given out by 1 gram of radium bromide per minute from September 1903 to January 1905 was 1.136 cals. E. W. W.

Relative Absorption of the Rays of Radium and Polonium. E. RIECKE [with RETSCHINSKY and WIGGER] (*Chem. Centr.*, 1905, ii, 1574—1575; from *Physikal. Zeit.*, 6, 683—685).—The results of determinations of the coefficients of absorption of the rays of radium and polonium should give a clue to the nature of the radiation. If, for instance, the radiation is effected by means of corpuscles, then the absorption-coefficient cannot be constant, since the absorption depends on the collision of the particles with the molecules of the absorbing substance, whilst, on the other hand, constant values should be obtained if the energy is transmitted by waves. Although, however, the absorption-coefficient of the α -rays of radium in air has been found to be constant, the deflection of the rays in a magnetic or electric field appears to indicate a corpuscular structure. Experiments on the α -rays of polonium, in which Marckwald's arrangement of a copper rod covered with radiotellurium was employed, have shown that the absorption-coefficient is not constant. The velocity of the rays is decreased by collision of the particles with the molecules of the air, whilst the absorption is increased. The results of experiments on the absorption of the γ -rays emitted by radium bromide in lead have proved that the

rays are not homogeneous ; their nature is not affected by the absorption. When a lead plate of sufficient thickness is used, only those rays which have the lowest absorption-coefficient (0.25) remain. The theory of the identity of the γ -rays with the Röntgen rays is supported by the fact that the absorption-coefficient of the "residual" rays in mercury, lead, copper, iron, zinc, aluminium, and sulphur is proportional to the sp. gr. of the substance ($k/d = 0.0021$). E. W. W.

Radioactivity of Products of Etna. GIOVANNI TROVATO CASTORINA (*Nuovo Cim.*, 1905, [v], 10, 198—202).—In general, the products of Etna are radioactive, the following series being in order of increasing activity: rock, sand, sandy tufa, clay and clayey soil, mud, soil and pozzolane, or soil coloured by the lava. The activity of the soil is influenced by heating, by chemical reactions, or by absorption of water. T. H. P.

A. E. Nordenskiöld's Investigations on the Radioactivity of certain Swedish and Norwegian Minerals. HJALMAR SJÖGREN (*Arkiv Kem. Min. Geol.*, 1905, 2, i, No. 4, 1—5).—The author gives an account of A. E. Nordenskiöld's researches on the radioactivity of Swedish and Norwegian minerals, which, in order of their activity, are as follows: cleveite from Raade; uraninite from Johannegeorgensstadt; orangite and yellow thorite from Svinör; nohlite from Nohl; fergusonite from Sandöen, and orangite from Brevig; euxenite from Mörefjär; æschynite from Hitterö; xenotime from Sandöen; monazite from Raade, and fergusonite from Ytterby; malacon from Kammerfors. Columbite from Moss, ixiolite from Skogböle, and hjelmite from Nya Kårarfvet showed no action on a sensitive plate even after ninety-six hours' exposure. The paper is accompanied by photographs illustrating the actions of the different minerals. T. H. P.

Abnormal Anodic Polarisation produced by Fluorine, Chlorine, and Bromine Ions. ERICH MÜLLER and ALFRED SCHELLER (*Zeit. anorg. Chem.*, 1905, 48, 112—128. Compare Abstr., 1904, ii, 250, 811, 812. Skirrow, Abstr., 1903, ii, 69).—It has already been shown by Müller and others that the addition of indifferent ions often causes increased polarisation at the anode (*loc. cit.*); in the present paper, the effect of fluorine, chlorine, and bromine ions on the anode potential during the electrolysis of sulphuric acid is described. Experiments were made with a series of mixtures of normal sulphuric acid and normal solutions of the halogen acids with different current densities and at various temperatures, and the results are represented by curves, the potentials being plotted as ordinates against the composition of the mixtures as abscissæ.

With hydrochloric acid at the ordinary temperature, the curves show maxima at about 2.5 per cent. of the acid; the greater the current density, the greater is the rise in potential and the more distinct the maximum. With very small current densities, the only effect of chlorine ions is to lower the potential. Increasing the temperature

has the same effect as lessening the current density ; thus, the chlorine ion has a powerful polarising action at 0° which quite disappears at 70° .

The bromine ion has a similar but less powerful action ; only mixtures containing less than 10 per cent. of the acid show increased potential, whereas stronger solutions lower it very considerably.

Hydrofluoric acid increases the anode potential in all concentrations ; in this case as well the effect decreases with rise of temperature.

It is pointed out that the above results are very similar to those obtained in investigating the decomposition potentials of the halogen acids (compare Luther and Brislee, *Abstr.*, 1903, ii, 708). The author suggests that the phenomena observed are due to the formation of the lower halogen oxyacids, and shows that this theory accounts for the results obtained with chlorine and bromine ions.

G. S.

Mechanism of the Production and the Nature of Cathodic Pulverisations. CH. MAURAIN (*Compt. rend.*, 1905, 141, 1223—1225).—When a plate of glass or mica is placed opposite or inclined to the cathode inside a tube containing a rarefied gas, the film of cathodic material which is deposited on it is most abundant at the edges, that is, at those parts of the plate farthest removed from the cathode. When the vacuum tube is placed between the poles of an electro-magnet in such a position that the cathode is normal to the magnetic field, the cathodic film deposited on the walls on the tube is most abundant in the trace of the luminescent plane and in a plane at right angles to it. From the results of these and similar experiments, the author draws the conclusion that the cathodic pulverisations are formed of fairly large particles torn from the cathode by the impact of the α -rays, projected in all directions, and carrying variable electrical charges, the e/m being much smaller than in the case of the particles forming the cathode rays.

M. A. W.

Chemical Composition of the Nickel Oxide Electrode in the Jungner Edison Accumulator. JULIAN ZEDNER (*Zeit. Elektrochem.*, 1905, 11, 809—813).—If nickelic oxide be prepared in any way and pasted on to a platinum wire, the potential difference between the wire and zinc amalgam in a solution of potassium hydroxide is the same as if the nickelic oxide were not present. A nickel oxide accumulator plate gives a larger potential difference, and nickelic oxide deposited electrolytically in various ways on platinum gives the same result as the accumulator plate. The negative result obtained with the pasted oxide is probably due to its extremely small conductivity. Quantities of nickelic oxide sufficient for analysis were obtained by electrolysing a solution of nickel sulphate and sodium acetate with a rapidly rotating anode and adding dilute alkali hydroxide solution gradually so as to maintain the solution constantly neutral. The substances obtained had compositions varying between those represented by the formulæ $\text{Ni}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $\text{Ni}_2\text{O}_3 \cdot 11\text{H}_2\text{O}$, according to the method of drying. Exact measurements of the *E.M.F.* of the cell $\text{Zn} \mid \text{Zn}(\text{OK})_2 + \text{KOH} \mid \text{Ni}_2\text{O}_3$ showed that this oxide is identical with that formed in the accumulator.

T. F.

Lead Peroxide as Anode in the Electrolytic Oxidation of Chromium Sulphate to Chromic Acid. ERICH MÜLLER and MAX SOLLER (*Zeit. Elektrochem.*, 1905, 11, 863—872).—Chrome alum, dissolved in *N*-sulphuric acid, is not appreciably oxidised to chromic acid when an anode of smooth platinum is used. Traces of a salt of lead in the solution are precipitated at the anode as lead peroxide and bring about considerable oxidation. Small quantities of chlorine ions also favour the change. The oxidation takes place at a platinised platinum anode to about one-third the extent observed under similar conditions with a lead peroxide anode. With a lead peroxide anode, the oxidation takes place almost quantitatively in fairly concentrated solutions of chrome alum when the current density is not too high (about 0.005 ampere per sq. cm. is suitable). The difference in the behaviour of the platinum and lead peroxide anodes is not due to the latter having a higher anodic potential (the reverse is rather the case), but appears to depend on a catalytic action of lead peroxide which is capable of producing the oxidation purely chemically. T. E.

Conductivity and Viscosity of Solutions of certain Salts in Mixtures of Acetone with Methyl Alcohol, Ethyl Alcohol, and Water. HARRY C. JONES and EUGENE C. BINGHAM (*Amer. Chem. J.*, 1905, 34, 481—554. Compare Jones and Carroll, *Abstr.*, 1905, ii, 73).—A study has been made of the relations between the viscosities and conductivities of lithium nitrate, potassium iodide, and calcium nitrate in mixtures of acetone with methyl alcohol, ethyl alcohol, and water.

Determinations have been made of the conductivity at 0° and 25° of solutions of these salts of various concentrations in methyl alcohol, acetone, ethyl alcohol, water, and mixtures of acetone with methyl alcohol, ethyl alcohol, or water containing 25, 50, or 75 per cent. of acetone. The results of the experiments are tabulated and plotted as curves. The temperature-coefficients have been calculated in all cases.

The viscosities at 0° of acetone, methyl alcohol, ethyl alcohol, and mixtures of methyl alcohol and acetone and of ethyl alcohol and acetone have been determined. Determinations have also been made of the viscosity at 0° and 25° of water, a mixture of water with 25 per cent. of acetone, and solutions of calcium nitrate in the following solvents: acetone, methyl alcohol, and mixtures of acetone with water, methyl alcohol, or ethyl alcohol containing 25, 50, or 75 per cent. of acetone. The viscosity, fluidity, and density of the various solutions are given in tabular form. The fluidities are also plotted as curves. Comparisons of the temperature-coefficients of conductivity and fluidity in these mixtures show that they vary in the same manner, but that the former are uniformly smaller than the latter.

The conductivities of the salt solutions in mixtures of acetone and water exhibited the minimum in conductivity which has been observed previously and which is shown to be intimately connected with the minimum in fluidity. In the mixtures of acetone and alcohols, the fluidities are in accordance with the law of averages and the fluidity curve is nearly a straight line, whence it is concluded that acetone and these alcohols do not form complex molecular aggregates when mixed.

The curves for the conductivity of potassium iodide in the various mixtures are nearly straight lines at all dilutions and are very similar to the corresponding fluidity curves. Lithium nitrate and calcium nitrate in mixtures of acetone with methyl or ethyl alcohol show a deviation from the fluidity curves and exhibit a pronounced maximum in conductivity. After a consideration of the various factors which could influence the conductivity, it was concluded that the observed maximum is due to a change in the dimensions of the atmospheres about the ions (compare Kohlrausch, *Abstr.*, 1903, ii, 403). The conclusion of Dutoit and Friderich (*Abstr.*, 1899, ii, 351) and of Jones and Carroll (*loc. cit.*) that conductivity is directly proportional to the dissociation and inversely proportional to the viscosity is incomplete, since it does not allow for possible changes in the size of the ionic spheres. The conductivities of lithium nitrate and calcium nitrate in mixtures of acetone and water also show a tendency towards a maximum. This tendency to form a maximum in conductivity increases from potassium iodide through calcium nitrate to lithium nitrate, and it is considered that this may be connected with the velocities of migration of the ions.

E. G.

Can an Element form both Positive and Negative Ions?

MAX LE BLANC (*Zeit. Elektrochem.*, 1905, 11, 813—818).—Both sulphur and selenium (in the form of a thin film on a platinum wire), when used as cathodes in potassium hydroxide solution, go into solution in the form of polysulphide or polyselenide ions, S_x^{--} or Se_x^{--} , the largest values of x observed being 5 and 4.4 respectively. Used as anodes, no action was observed at all. Tellurium as cathode in alkaline solutions dissolves readily; in very concentrated solutions of potassium hydroxide, the dust observed by Müller and Lucas (*Abstr.*, 1905, ii, 672) is not formed. Its formation is more probably due to the dissociation of polytelluride ions, $Te_2^{--} \rightleftharpoons Te^{--} + Te$ in dilute solutions. At a tellurium anode in potassium hydroxide, there is no visible change, but tellurium goes into solution with the valency 3.9; it therefore gives off the ions $Te^{3.9--}$, which then react with hydroxyl ions to form the ions TeO_3^{--} .

T. E.

Experimental Study of the Three Parts of an Electrolytic Cell and their Relationships. G. HOSTELET (*Zeit. Elektrochem.*, 1905, 11, 889—904).—In determining decomposition points by Glaser's method (*Abstr.*, 1899, ii, 78), the author found difficulty in interpreting the results owing to variations in the resistance of the system and in the potential of the constant electrode. He has therefore worked out a method in which the falls of potential between the anode and the electrolyte, between the cathode and the electrolyte, and in the electrolyte itself, are all separately and simultaneously determined. The method is applied to the study of the electrolysis of potassium chloride with a platinum anode and a cathode of mercury.

T. E.

Theory of Electrolytic Dissociation, taking account of the Electrical Energy. R. MALMSTRÖM (*Zeit. Elektrochem.*, 1905, 11, 797—809).—In addition to the ordinary attractions between the

various molecules in the solution of an electrolyte, there are forces due to the attractions and repulsions of the electric charges on the ions. Assuming these electrical forces to be superposed on the ordinary attractive forces, the free energy of a dissolved electrolyte is calculated, and from this an equation for the equilibrium between the ions and undissociated molecules is obtained. This is found to be in rather better agreement with measurements of conductivity than any of the equations proposed previously. It is suggested that, owing to electrostriction, the dielectric constant of the solution must be a function of the concentration and that a better agreement might be obtained by taking this into account. T. E.

Theory of Electrolytic Dissociation. LOUIS KAHLENBERG (*Phil. Mag.*, 1905, [vi], 10, 662—664. Compare Abstr., 1905, ii, 139).—A reply to Jones' criticism (*Phil. Mag.*, 1905, [vi], 10, 157).

J. C. P.

Accurate Measurement of Ionic Velocities. ROBERT B. DENISON and BERTRAM D. STEELE (*Proc. Roy. Soc.*, 1905, 76 A, 556—557).—An apparatus has been devised for measuring the velocities of ions without using gelatin or other partitions during the experiment. The apparatus consists of two reservoirs, each provided with a special electrode vessel, and of a measuring tube of known cross-section in which the solution to be examined is placed. One of the reservoirs contains a solution of a salt with a less mobile cation than the cation under observation, the other a solution of a salt with a less mobile anion than that of the salt under investigation. The measuring tube is provided at each end with parchment-paper partitions which facilitate the formation of a sharp electrolytic margin between the measured and the indicator solutions, and these partitions are so arranged that they can be removed after the margins have been formed. Experiments have been made at dilutions down to 0.02 normal. The calculated transport numbers agree very well with those obtained by Hittorf's method, and the measured average ionic velocities confirm in a remarkable manner those calculated from conductivity data.

H. M. D.

Mobility of Ions of Salt Vapours. GEORGES MOREAU (*Compt. rend.*, 1905, 141, 1225—1227. Compare Abstr., 1903, ii, 125, 196; 1904, ii, 536; 1905, ii, 9).—The author has measured between the temperatures of 170° and 15° the mobility (k) of the ions in air which has been bubbled through solutions of potassium salts of different concentrations and then passed through a tube heated to redness. From the values of k thus obtained, the sizes of the ions for different temperatures and concentrations are calculated, with the results that at the higher temperatures the ions have a diameter five to fifteen times that of the molecule, and appear to consist of an electrically charged nucleus surrounded by two to seven layers of molecules, whilst at the lower temperatures the number of layers is increased to ten to twenty.

M. A. W.

Electrical Conductivity of Dilute Solutions of Sulphuric Acid. W. C. DAMPIER WHETHAM (*Proc. Roy. Soc.*, 1905, 76 A, 577—583).—The equivalent conductivity of solutions of strong acids and alkali hydroxides increases with dilution, but reaches a maximum at 0.001 to 0.0005 gram-equivalent per litre, and falls rapidly with further increase in dilution. The effect of traces of impurities on the equivalent conductivity of sulphuric acid in dilute solution has been examined by measuring the variation of the conductivity with the concentration in four solvents: (1) good quality redistilled water, and the same containing (2) a trace of carbon dioxide, (3) a trace of potassium chloride, and (4) the same water freed as far as possible from volatile impurities by repeated boiling under diminished pressure. In each case, the conductivity of the solvent was subtracted from that of the solution. The results show that the conductivity of sulphuric acid in dilute solution is not affected by addition of a trace of potassium chloride or by boiling under diminished pressure, but that it is appreciably diminished in presence of a little carbon dioxide, and in this case the maximum conductivity is reached at a higher concentration. The abnormally low conductivity of dilute solutions cannot, however, be wholly attributed to the presence of carbon dioxide in the water used as solvent.

H. M. D.

Transit of Ions in the Electric Arc. A. A. CAMPBELL SWINTON (*Proc. Roy. Soc.*, 1905, 76 A, 553—556).—An experiment has been devised to show that the current in the electric arc is carried by positive and negative ions emitted by the electrodes. A small hole was bored axially through one of the carbon electrodes, which was fixed rigidly at the end of a brass tube, and an insulated Faraday cylinder was supported within the brass tube so that its aperture was in line with and immediately behind the aperture in the carbon electrode. With a current of three amperes and about 50 volts, the Faraday tube remained unchanged in atmospheric air, but when the apparatus was enclosed in a glass vessel and the pressure reduced, the Faraday cylinder acquired the same charge as the opposite carbon electrode. The effect increased with the degree of exhaustion of the containing vessel, and, corresponding with the greater mobility of the negative ions, the galvanometer deflection for a given degree of exhaustion was greater when the opposite carbon electrode was made the negative pole.

H. M. D.

Magnetisation and Magnetic Change of Length in Ferromagnetic Metals and Alloys at Temperatures ranging from -186° to $+1200^{\circ}$. KÔTARÔ HONDA and SUMU SHIMIZU (*Phil. Mag.*, 1905, [vi], 10, 642—661).—The paper contains a large number of data bearing on the magnetisation of Swedish iron, nickel, annealed cobalt, and various nickel steels. The results obtained are in general harmony with those of earlier observers, such as Osmond and Dumas.

J. C. P.

Coexistence of Paramagnetism and Diamagnetism in the same Crystal. GEORGES MESLIN (*Compt. rend.*, 1905, 141, 1006—1008. Compare *Compt. rend.*, 1905, 140, 1683).—A small

cube cut from a crystal of pyrrhotite in such a way that its faces are parallel with or perpendicular to the magnetic plane exhibits paramagnetism when placed in a magnetic field in such a position that the magnetic plane passes through the axis of the electro-magnet, whilst in a direction at right angles to this it exhibits diamagnetism. By immersing the cube in a concentrated solution of ferric chloride, its paramagnetic susceptibility is diminished and its diamagnetic susceptibility is increased.

M. A. W.

Magnetic Compounds of Non-magnetic Elements. EDGAR WEDEKIND (*Zeit. Elektrochem.*, 1905, 11, 850—851).—The manganese borides previously described (Abstr., 1905, ii, 322) are found to be strongly magnetic; they also possess considerable permanent magnetism. Compounds of manganese with antimony and bismuth are also magnetic; manganese arsenide, however, is not magnetic but becomes magnetic when heated in the air. The phosphides, carbides, and sulphides of manganese, prepared by the alumino-thermic process, are also magnetisable, whilst the silicide is not so.

T. E.

Specific Heats of Gases. SILVIO LUSSANA (*Nuovo Cim.*, 1905, [v], 10, 192—195).—The author points out that, although in their paper on the specific heats of gases at high temperatures Holborn and Austin (Abstr., 1905, ii, 228) affirm that it is impossible to state with certainty that the specific heats of the simple gases increase as the temperature rises, yet all their results exhibit such an increase, the mean value of which is 3 per cent., whilst the accuracy of their measurements is about ± 1 per cent.

The author's investigations on this subject, extending over a number of years, lead to the conclusions that for all gases the specific heat at constant pressure (1) increases with the pressure up to a certain limiting value and then diminishes, the maximum corresponding with a pressure which is lower as the gas deviates more from Boyle's law, and (2) increases or diminishes with the temperature according as the latter is near to or far from the temperature of liquefaction of the gas; the temperature variation of the specific heat increases with the pressure.

T. H. P.

Latent Heat of Fusion of Ice. ANATOLE LEDUC (*Compt. rend.*, 1906, 142, 46—48).—There is a difference of nearly 1 per cent. between Bunsen's value (80.03) for the latent heat of fusion of ice and the value (79.25) found by Laprovostaye and Desains and confirmed by Regnault, and the difference is still of the same order if the numbers are corrected for the variation of the specific heat of water, taking 1.004 as the specific heat of water at 0° according to the results obtained by Callendar and Barnes. If, however, the author's value, 0.9176, for the specific volume of ice at 0° is substituted for the value found by Bunsen, 0.91674, Bunsen's value for the latent heat of fusion of ice becomes 79.15, and the author considers that 79.2 is the most probable value for this constant.

M. A. W.

Connection between Depression of Freezing Point and Latent Heat of Fusion. KARL DRUCKER (*Zeit. Elektrochem.*, 1905, 11, 904—905).—Goebel (Abstr., 1905, ii, 679) has calculated the latent heat of fusion of ice at temperatures below zero from the vapour pressures of ice and water. The author points out that a very small inaccuracy in the formula representing the vapour pressures makes a very large error in the heats of fusion calculated. Goebel's results differ enormously from Pettersson's direct determinations. If the latter are used to calculate the vapour pressures of ice, numbers are obtained in good agreement with the experimental numbers. Hence the correction of the freezing-point depressions given by Goebel is much too large. He has also, erroneously, taken the concentrations in gram-molecules per litre of solution instead of per kilogram of water, which partially compensates the first error. T. E.

Solvent and Ionising Properties of Ethylene Cyanide (Succinonitrile). GIUSEPPE BRUNI and ANTONIO MANUELLI (*Zeit. Elektrochem.*, 1905, 11, 860—862).—The molecular depression of the freezing point of succinonitrile is 182.6, from which the molecular latent heat of fusion is calculated to be 0.94 cal., which is the smallest value yet observed for any organic compound. Ethylene bromide and chloride give abnormally small depressions of freezing point when dissolved in succinonitrile, which is doubtless due to the formation of solid solutions. Compounds containing amino- or hydroxyl groups give small depressions, probably owing to molecular association. The high dielectric constant of succinonitrile points to considerable dissociating power. The freezing points of solutions of potassium and tetraethylammonium iodides were determined and values of i calculated which lie between 1.26 and 1.3 for potassium iodide and 1.78 and 1.89 for tetraethylammonium iodide. The latter solutions conduct well. The anhydrous chlorides of copper, manganese, cobalt, and nickel are insoluble in succinonitrile. T. E.

Critical Temperature of Solutions in Liquid Carbon Dioxide. ERNST H. BÜCHNER (*Chem. Centr.*, 1905, ii, 1618—1619; from *Chem. Weekblad*, 2, 691—694).—The results of experiments on solutions of *p*-dichlorobenzene, tribromomethane, *p*-dibromobenzene, *o*-chloronitrobenzene, naphthalene, and 1:3-dichloro-5-nitrobenzene in liquid carbon dioxide have shown that van't Hoff's law holds approximately in these cases, the molecular rise of the critical temperature being almost constant. The results may, however, be more accurately expressed by means of van Laar's hypothesis, in which the rise per gram-molecule per cent. is not only dependent on the critical temperature of the solvent, but also on the relationship of the critical temperature of the dissolved substance to that of the solvent and on the ratio, π , of the critical pressures. Since, as a rule, $\pi = 1$, $\delta = \theta(\theta - 1)$, in which $\delta = 1/T_k \cdot (dT_x/dx)$ and T_k = critical temperature of the solvent.

E. W. W.

Relative Vapour Tensions of the Three Modifications of Carbon. ANDREAS SMITS (*Ber.*, 1905, 38, 4027—4033. Compare Schenck and Heller, Abstr., 1905, ii, 519).—The equilibrium constant

of the reaction $\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$ is $K_1 = p^2_{\text{CO}}/p_{\text{CO}_2}p_{\text{C}}$, where p_{C} is the partial vapour pressure of the carbon, that is, the maximum vapour pressure of the solid carbon at the given temperature. As this increases, so do the values of K_1p_{C} and $p^2_{\text{CO}}/p_{\text{CO}_2}$ in the equation $K_1p_{\text{C}} = p^2_{\text{CO}}/p_{\text{CO}_2}$. The equilibrium constant for the reaction $\text{Fe} + \text{CO}_2 \rightleftharpoons \text{FeO} + \text{CO}$ is $K = (p_{\text{CO}} \cdot p_{\text{FeO}})/(p_{\text{CO}_2} \cdot p_{\text{Fe}})$; if the differences in the solubilities of the three modifications of carbon in iron are neglected, $p_{\text{FeO}}/p_{\text{Fe}}$ may be considered as constant, and the equation may be written $K_2 = p_{\text{CO}}/p_{\text{CO}_2}$. If the sum of the partial vapour pressures $\text{CO} + \text{CO}_2 = P$, then $P = k_1p_{\text{C}}(1 + k_2)/k_2^2$, which differs from Schenck and Heller's equation by the presence of p_{C} (*loc. cit.*), and the greater the vapour pressure of the modification of carbon the greater is the equilibrium pressure P . If p_{C} , p'_{C} , and p''_{C} are the vapour pressures of the three modifications, then $P : P' : P'' = p_{\text{C}} : p'_{\text{C}} : p''_{\text{C}}$.

The author discusses the work of Schenck and Heller from a theoretical point of view and concludes that the equilibrium pressures measured by them are not trustworthy. If, however, these are assumed to be correct, the vapour pressures of the diamond, amorphous carbon, and graphite are in the proportions: $p_{\text{C}} : p'_{\text{C}} : p''_{\text{C}} = 3.7 : 1.8 : 1$ at 500° ; $4.1 : 2.4 : 1$ at 550° ; $5.2 : 4.1 : 1$ at 600° ; and $5.4 : 4.2 : 1$ at 641° .
G. Y.

Distillation in High Vacua by means of Dewar's Air Absorption Method, and a Shortened MacLeod Vacuum Gauge. ALFRED WOHL and M. S. LOSANITSCH (*Ber.*, 1905, 38, 4149—4154. Compare Fischer and Harries, *Abstr.*, 1902, ii, 491; Erdmann, 1904, ii, 20).—The apparatus, to which is attached an absorption vessel containing 20—30 grams of extracted blood charcoal, is evacuated by means of an ordinary water pump, and the receiver and absorption vessel are then cooled by liquid air. Pressures of 0.006—0.008 mm. can thus be attained within thirty minutes. It is not necessary that the apparatus shall be absolutely air-tight, as small amounts of air which enter are absorbed by the charcoal. The same cooled charcoal (25—30 grams) may be used for several distillations, provided the apparatus is exhausted before being attached to the absorption vessel.

For measuring high vacua, a MacLeod apparatus shortened in much the same manner as suggested by Stock (*Abstr.*, 1905, ii, 514) for the Töpler mercury pump is recommended.
J. J. S.

Distillation of Liquids which are Mutually Insoluble. C. VON RECHENBERG and W. WEISSWANGE (*J. prakt. Chem.*, 1905, [ii], 72, 478—488).—Experiments on the weights of the two components of a non-miscible liquid mixture which distil over are not in accord with the conclusions of Charabot and Rocherolles (*Abstr.*, 1904, ii, 234). The authors' results are, however, in accord with their deductions that the weights of the components are proportional to the products of their molecular weights and partial pressures. If the vapour mixture is saturated with respect to both components, then the partial pressure for each component is the normal vapour pressure corresponding with the temperature of the vapour. If the vapour mixture is unsaturated

with respect to one component, the unsaturated vapour has the pressure equal to the difference between the pressure of the mixed vapour and the vapour pressure of the saturated component at the temperature of the mixed vapour.

L. M. J.

Progressive Dissociation of Dibasic Acids. II. RUDOLF WEGSCHEIDER (*Monatsh.*, 1905, 26, 1235—1239. Compare Abstr., 1902, ii, 643).—In the case of sparingly soluble dibasic acids or of those which have a high value for the dissociation constant s of the second hydrogen atom, it is necessary to calculate both dissociation constants from the results of the same experiments, which may be done if approximate values for the two constants are known or can be guessed. A maximum value for k , the dissociation constant of the first hydrogen atom, is obtained according to Ostwald's law of dilution from the conductivity in the most concentrated solution.

If the value (I) $\frac{\mu - 2g_2(l_K + l_{2A})}{\mu_\infty}$ is substituted for g_1 in the equations (1) and (2) previously given, then (II)

$$g_2 = \frac{2sv(l_K + l_{2A}) + \mu}{4(l_K + l_{2A} - \mu_\infty)} \left(1 - \sqrt{1 - \frac{8sv\mu(l_K + l_{2A} - \mu_\infty)}{[2sv(l_K + l_{2A}) + \mu]^2}} \right),$$

in which g_2 is a function of the known constants l_K , l_{2A} , and μ_∞ of the experimentally determined values v and μ and of the unknown constant s , and (III) $F(k_1s) = kv\mu_\infty \{ \mu_\infty - \mu + g_2[2(l_K + l_{2A}) - \mu_\infty] \} - [\mu - 2g_2(l_K + l_{2A})][\mu - 2g_2(l_K + l_{2A} - \mu_\infty)] = 0$, where F is a function of k and s .

If the approximate value of k and the values of g_2 calculated by equation (II) from the results of a number of experiments with assistance of the approximate value of s are substituted in equation (III), as many values of F are obtained, and the values of k and s must be altered until in each case $F=0$. If $k + \delta k$, $s + \delta s$ are the correct values for the two constants k and s , then (IV) $0 = F(k + \delta k, s + \delta s) = F(k, s) + \frac{\delta F}{\delta s} \delta s + \frac{\delta F}{\delta k} \delta k$; from these are obtained two

equations by means of which δk and δs may be calculated. Equations are given also for the adjustment of s and k in case of more than two observations.

The method of calculation is illustrated in the case of 4-acetylaminoisophthalic acid.

G. Y.

Dissociation of Electrolytes. CARL HENSGEN (*J. prakt. Chem.*, 1905 [ii], 72, 345—477).—It has been shown previously that concentration differences exist in a salt solution not entirely at the same temperature. This case is first investigated for a solution of copper sulphate, the upper layer of which was kept at a temperature of about 98°, whilst the lower was maintained at the ordinary temperature. It was found that not only was the concentration different for the two layers, but also that the ratio $\text{CuO} : \text{SO}_3$ was not unity, and was greatest for the highest layer. Numerous expressions have at different times been proposed to connect the sp. gr. of a solution with its chemical composition; these are fully considered, and found by the author to be unsatisfactory for solutions of copper sulphate, and it is

found that the ratio $\text{CuO} : \text{SO}_3$ varies within wide limits. Numerous tables, showing this ratio at different temperatures and concentrations, are given in the paper and fully discussed. The author considers that his results indicate that solutions of normal salts are the liquid phases of a heterogeneous equilibrium system, brought about by the chemical action of the water and dependent on temperature, &c. The general idea associated with the term solution of a normal salt, namely, the complete passage of the solid normal salt into the solution, maintaining throughout the same proportion of its components regarded as base and acid, is not consistent with the actual conditions. The molecular contents of normal salts in solution are, therefore, not calculable. Crystallisation of normal salts takes place only in solutions which do not contain acid and base in the same proportions as those of the precipitated salt. It is evident that these conclusions are not in accord with ordinary chemical views of solution, and they and their consequences are discussed at considerable length by the author in the paper (compare Abstr., 1901, ii, 540). L. M. J.

Molecular Weight of the Solvent in Binary Mixtures. KARL DRUCKER (*Zeit. Elektrochem.*, 1905, 11, 845).—The author assumes that the surface tension of a binary mixture may be expressed on the analogy of van der Waals' molecular attraction constant by $1/\gamma = 1/\gamma_1 x^2 + 1/\gamma_2 (1-x)^2 + 1/\gamma_{1.2} (1-x)x$. The formula is applicable to mixtures of non-associating substances; $\gamma_{1.2}$ becomes constant in mixtures of acetic acid and benzene or carbon tetrachloride when the molecular weight of acetic acid is taken as double its formula weight; in mixtures of water with alcohols or fatty acids, constancy of $\gamma_{1.2}$ is obtained by trebling or quadrupling the molecular weight of water. T. E.

Origin of the Formation of Layers in Solutions observed by A. Sinding-Larsen. C. CHRISTIANSEN (*Chem. Centr.*, 1905, ii, 1617; from *Overs. K. Danske Vidensk. Selsk. Forh.*, 1905, 307—315).—Sinding-Larsen (*Ann. Physik*, 1903, [iv], 9, 1186) observed that when solutions of sodium chloride in which the concentration was not uniform were heated, sharply defined layers were formed, and attributed the cause to surface tension and the formation of hydrates. Experiments on water, water and toluene, and with various solutions have shown, however, that layers may be formed by heating the liquids on one side and cooling them on the other. The formation of layers is due to movement of the liquid and to differences of temperature, and is in no way dependent on the formation of hydrates. The surface of contact between two layers of different concentrations can only remain sharply defined when the liquid is in motion, and although the mixture of the layers is thereby delayed it is not entirely prevented. An electrolytic method of causing two layers of sulphuric acid solutions to circulate is also described in the original paper. E. W. W.

Limiting States of some Dissolved Chromic Salts. ALBERT COLSON (*Compt. rend.*, 1905, 141, 1024—1027. Compare Abstr., 1905, ii, 94, 255, 460, 592).—When a solution of the normal green chromic

sulphate, $\text{Cr}_2(\text{SO}_4)_3$, is exposed to sunlight, the colour becomes turquoise-blue, the density increases (compare Boisaudran, Abstr., 1875, 427, 730), and the heat of decomposition by potassium hydroxide diminishes to a limiting value reached more rapidly in dilute than in more concentrated solutions, as is shown in the following table :

Duration of exposure to sunlight.	Heat of decomposition $[\text{Cr}_2(\text{SO}_4)_3:6\text{KOH}]$.	
	Solutions of 1/10 mol. per litre.	Solutions of 3/10 mol. per litre.
0	57,200 cal.	57,200 cal.
10 days (May)	—	56,100 „
28 „	51,600 „	—
48 „	50,400 „	—
84 „	50,100 „	52,200 „
165 „	50,100 to 50,000 cal.	51,800 „

The change in density corresponds with a contraction of 1 mol. H_2O per 1 mol. $\text{Cr}_2(\text{SO}_4)_3$, and the turquoise-blue solution probably contains the hydrated sulphate, $\text{SO}_4 < \begin{smallmatrix} \text{Cr}(\text{OH}) \cdot \text{SO}_4\text{H} \\ | \\ \text{Cr} : \text{SO}_4 \end{smallmatrix}$, of which the heat of decomposition by potassium hydroxide is 50,000 cal., and not an equilibrium mixture of the green and violet chromic sulphates, of which the heat of decomposition would be $(57,200 + 45,000)/2$ cal. or 51,100 cal.

A solution of the violet chromic acetate, $\text{OCr}_2(\text{OAc})_4$, in excess of acetic acid becomes green on exposure to sunlight, and cryoscopic and thermochemical measurements indicate that the tetra-acetate has combined with acetic acid to form the penta-acetate, $\text{OH} \cdot \text{Cr}_2(\text{OAc})_5$, which, however, cannot be isolated, for on evaporating the green solution to dryness it decomposes into the two salts $\text{Cr}(\text{OAc})_3$ and $\text{OH} \cdot \text{Cr}(\text{OAc})_2$.
M. A. W.

Abnormal Increase of Solubility with Organic Substances.

DANIEL STRÖMHOLM (*Arkiv Kem. Min. Geol.*, 1905, 2, i, No. 7, 1—9).—The author has examined the influence of the addition of small quantities of water on the solubility in ether of benzoic acid, *p*-nitrobenzoic acid, picric acid, acetanilide, quinol, phloretin, methyl terephthalate, benzil, β -naphthaquinone, phthalimide, α -nitronaphthalene, *p*-nitroaniline, β -naphthylamine, benzyl sulfoxide, sulphonol, benzyl sulphide, azobenzene, and phenanthrene. The presence of water in excess causes the solubility in ether to increase by the following percentage proportions: benzoic acid, 80; quinol, 296; α -nitronaphthalene, 10.5; methyl terephthalate, 16.7; benzil, 19; β -naphthaquinone, 43; β -naphthylamine, 33.3; *p*-nitrobenzoic acid, 161; picric acid, 573; acetanilide, 517; *p*-nitroaniline, 127; phthalimide, 47.7; benzyl sulfoxide, 92.2; and sulphonol, 30.2. With benzyl sulphide, azobenzene, and phenanthrene, the increases in solubility are inappreciable.

Augmentation of the solubility hence occurs with all the acid substances examined and with all non-acid compounds containing amino-groups. Hydroxyl compounds, carboxylic acids, and phenols appear to be very greatly influenced.

In the cases of mercuric chloride and iodine, the author has previously shown (Abstr., 1903, ii, 547 and 644) that the increase of solubility caused by addition of water is due to the existence of hydrates of these substances in solution. This is probably also the case with the above-mentioned compounds. T. H. P.

Partition of some Organic Acids between Two Solvents. WALTER HERZ and MARTIN LEWY (*Zeit. Elektrochem.*, 1905, 11, 818—820).—The partition of acetic, chloroacetic, and picric acids between water on the one hand and chloroform, bromoform, carbon disulphide, and carbon tetrachloride on the other hand is studied. The results point to the existence of double molecules in the more dilute solutions and of more complex molecules in the more concentrated solutions. T. E.

Passivity of Metals. WOLF J. MÜLLER (*Zeit. Elektrochem.*, 1905, 11, 823—824).—The author's theory of passivity was incorrectly stated by Ruer (Abstr., 1905, ii, 795). T. E.

Passivity. CARL FREDENHAGEN (*Zeit. Elektrochem.*, 1905, 11, 857—860).—With special reference to Ruer's recent work (Abstr., 1905, ii, 795), the author maintains the view that passivity is better explained by assuming a protecting layer of gas (Abstr., 1903, ii, 353) than by assuming a skin of oxide. The gas theory is capable of accounting for cathodic as well as anodic passivity. The protecting layer of gas may exist as a solid solution, as a surface film, or in some intermediate condition. T. E.

Rate of the Reaction between Arsenious Acid and Iodine in Acid Solution; Rate of the Reverse Reaction; and the Equilibrium between them. (II.) J. R. ROEBUCK (*J. Physical Chem.*, 1905, 9, 727—763. See Abstr., 1903, ii, 14).—It has been shown previously that the velocity of the reverse reaction is given by $dx/dt = K(\text{arsenic acid})(\text{pot. iodide})^a(\text{sulphuric acid})^\beta$, where a and β approach unity in dilute solution. The investigation of this was extended and the values a and β found to increase considerably with increasing concentration, values as high as 2.4 and 3.7 being obtained. Where the concentration of iodide (C) and acid (D) considerably exceeds that of the arsenic acid, the expression may be written $dx/dt = K_5 C D V^{-3}(E - x)$, and it was found that the value of K_5 increases as equilibrium approaches and also when dx/dt is decreased by decreasing $(E - x)$. The author considers that these anomalous results may be explained by the supposition that the reaction proceeds in two stages, namely: (1) $\overset{+}{\text{H}} + \overset{-}{\text{I}} + \text{H}_3\text{AsO}_4 = \text{H}_3\text{AsO}_4\text{HI}$, and (2) $\text{H}_3\text{AsO}_4\text{HI} = \text{H}_3\text{AsO}_3 + \text{HIO}$, the reaction of the first proceeding with a measurable velocity. The author extends his determination of the direct rate to near the equilibrium point, and from the reaction velocities in the neighbourhood of the equilibrium calculates the equilibrium constant, which agrees well with that directly determined, the two values being 1.4×10^5 and 1.5×10^5 . The temperature-coefficient

between 10° and 0° for the equilibrium constant was found to be 1.41 and that calculated from the coefficients of the direct and reverse velocities was 1.43. Experiments were also made with hydriodic acid in place of sulphuric acid, and results in accord with theory were also obtained.

L. M. J.

Affinity Constants of Amino-acids. RUDOLF WEGSCHEIDER (*Monatsh.*, 1905, 26, 1265—1276. Compare Abstr., 1902, ii, 494; Walker, Abstr., 1904, ii, 309; 1905, ii, 138).—The observed "acid" dissociation constant K of an amino-acid is less than the constant k_1 calculated from simple stoichiometric relations for those acids which obey Ostwald's law of dilution, or by means of Walker's constant for the "acid" dissociation of amphoteric electrolytes which do not obey the law of dilution, if an intramolecular salt is formed, or if the amino-group forms with water an ammonium hydroxide which is less negative, but is greater if the ammonium hydroxide is more negative than the amino-group.

If k', k'', \dots are the true constants of the "acid" dissociation of different acids having an amino-group in the same position relatively to the carboxyl, and x', x'', \dots are the dissociation constants of the corresponding acids with hydrogen in the place of the amino-group, then (1) $k_1'/x_1' = k_1''/x_1'' = \dots = f$, where f is the factor representing the influence of the amino-group. In a dibasic acid, which has x_1 and x_2 , the dissociation constants of the two carboxyl groups,

$$(2) k_1 = f_1 x_1 + f_2 x_2,$$

where f_1 and f_2 are the factors representing the influence of the two amino-groups, which are usually in different positions. As the observed constant (3) $K = k_1 \beta$, for monobasic acids

$$K'/x' = K''/x'' \dots = F,$$

and it follows from (1) and (3) that (4) $F = f\beta' = f\beta'' = \dots$. For dibasic acids, $K = F_1 x_1 + F_2 x_2$.

From (2), (3), and (4) it follows that

$$k_1 \beta = f_1 \beta_1 x_1 + f_2 \beta_2 x_2 = (f_1 x_1 + f_2 x_2) \beta.$$

As in this equation f and x can be realised only if $\beta = \beta_1 = \beta_2$, β must be the same for all amino-acids the affinity constants of which can be calculated by means of the same factor for the influence of the amino-group, irrespective of the position of the amino-group relatively to the carboxyl.

The constants K observed for acetylaminoterephthalic acid, 0.098, for 1-methyl hydrogen 3-acetylaminoterephthalate, 0.07, and for 4-acetylaminosophtalic acid, 0.079, agree moderately well with the constants calculated, 0.084, 0.066, and 0.069 respectively, with the aid of Ostwald's factors for the influence of the group NHAc in *o*-, *m*-, and *p*-acetylaminobenzoic acids.

The β -anilino-fatty acids, which are weak acids, give no constant factors, whereas the stronger α -anilino-acids give only small variations from the mean factors, for the anilino-group, 2.1, for the *p*-toluidino-group, 0.63, and for the *o*-toluidino-group, 3.3.

For the introduction of the acetylanilino-group, $\cdot\text{NPhAc}$, into the α -position of acetic, propionic, and butyric acids, the factors are 14, 9.4, and 7.3; for the introduction of the *o*-acetyltoluidino-group

into the α -position of the same acids, the factors are 12, 7.8, and 6.2; and for the introduction of the *p*-acetyluluidino-group into the α -position of acetic, propionic, butyric, and isobutyric acids the factors are 12, 7.8, 7.2, and 6.6 respectively. These factors are highest for the introduction of the groups into a methyl, lowest for introduction into a methenyl group.

The factors for the influence of the amino-group in the ortho-, meta-, and para-positions obtained from the three aminobenzoic acids, 0.17, 0.27, and 0.20 respectively, are much smaller than the factors obtained from 5-nitro-3-aminobenzoic acid, which gives $f(\text{NH}_2, m) = 0.61$, from 1-methyl hydrogen 3-aminoterephthalate, which gives

$$f(\text{NH}_2, o) = 0.33,$$

and from aminoterephthalic acid, which gives $f(\text{NH}_2, o) = 0.33$ and $f(\text{NH}_2, m) = 1.38$. The amino-group appears in some cases as a negative substituent, and it may be that in all other cases the smallness of the factor is due to salt formation. G. Y.

Theory of Dyeing. IV. Lakes. WILHELM BILTZ [with KURT UTESCHER] (*Ber.*, 1905, 38, 4143—4149. Compare Abstr., 1904, ii, 392; 1905, ii, 807, 808).—Experiments have been made by dyeing precipitated metallic hydroxides with alizarin and similar dyes. The results are arranged as curves in which the concentration of the dye-bath is plotted against the number of grams of dye taken up by one gram of hydroxide.

With ferric hydroxide and an alkaline solution of alizarin, the curve points to the formation of a definite compound of 1 mol. of hydroxide with 3 mols. of dye. The curve also indicates a certain amount of adsorption.

With chromic hydroxide and alizarin-red SW, the curve indicates adsorption and not chemical combination.

In the case of ferric hydroxide, the quantity of dye taken up depends to a large extent on the nature of the hydroxide; when gelatinous, some ten times as much dye is absorbed as when in the granular state.

Experiments with ferric hydroxide and alizarin in ammoniacal or alcoholic solution, with the same hydroxide and aqueous solutions of acid alizarin-blue and with aluminium hydroxide and alcoholic gallein solution gave no very definite results. J. J. S.

[Construction of the Periodic System.] AUGUSTO PICCINI (*Gazzetta*, 1905, 35, ii, 417—421).—The author criticises adversely the periodic system of the elements deduced by Werner (Abstr., 1905, ii, 308). T. H. P.

An Automatic Steam Generator and Superheater. JOHANNES THIELE (*Zeit. anal. Chem.*, 1905, 44, 767—768).—The apparatus consists of a vertical boiler having a conical opening down its centre. In this opening is placed a cylindrical vessel. The water is boiled by a burner under the boiler and the steam passes through a pipe into the upper part of the cylindrical vessel. The burner is now placed under the latter, from which the superheated steam is withdrawn by a pipe

reaching to the bottom of the vessel. The burner is regulated by a specially constructed thermostat which, by means of a side-tube, is not brought into action until the water in the boiler is at a boiling temperature.
W. P. S.

New Apparatus for the Extraction of Liquids. EFISIO MAMELI (*Chem. Centr.*, 1905, ii, 1569; from *La Sardegna Sanitaria*, 1). —An apparatus is described which only differs from a Soxhlet extraction cylinder in the following respects. The tube which conveys the vapour of the solvent from the flask is not sealed on to the side of the cylinder, but is connected with another tube which passes through the cork and reaches to the bottom of the cylinder. The siphon tube is lengthened so that it terminates near the bottom of the flask.

In another form, a small tubulus is attached to the bottom of the cylinder, through which a tube passes to the bottom of the flask, reaching to a convenient height in the cylinder and being straight or bent in the upper portion into a U form. The vapour of the solvent passes through a tube fitted in the cork of the flask and connected with the extraction cylinder as described above.
E. W. W.

Inorganic Chemistry.

Determination of the Density of Chlorine. FREDERICK P. TREADWELL and W. A. K. CHRISTIE (*Zeit. angew. Chem.*, 1905, **18**, 1934—1935).—A series of careful experiments gives for chlorine as a mean the density 2·488 at 20° and 730 mm. pressure and 2·489 at 10° and 725 mm. pressure.

One gram-molecule of chlorine at 0° and 760 mm. occupies a volume of 22,042 c.c. L. DE K.

The System: Perchloric Acid and Water. H. J. VAN WIJK (*Zeit. anorg. Chem.*, 1905, **48**, 1—52. Compare Abstr., 1902, ii, 649; Roscoe, *Annalen*, 1861, **121**, 346).—From the freezing-point curve of mixtures of perchloric acid and water, and from analysis of the crystals separating from the solutions on cooling, it has been shown that six well-defined hydrates exist, the respective formulæ and melting points of which are follows: $\text{HClO}_4 \cdot \text{H}_2\text{O}$, m. p. 50°; $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$, m. p. -17·8°; $\text{HClO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, m. p. -29·8°; two hydrates of the formulæ $\text{HClO}_4 \cdot 3\text{H}_2\text{O}$, melting at -37° and -43·2° respectively, and $\text{HClO}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ melting at -41·4°. The pure acid melts at about -112°. It has further been found that between certain limits of concentration and temperature two series of mixed crystals separate, the curves of which show maxima at about 78 and 85 mol. per cent. of water respectively. The eutectic mixture of the acid and water contains 88·7 mol. per cent. of the latter and solidifies at -57·5°.

The boiling-point curve of the system shows a maximum at 203° and 72.4 per cent. by weight of water. The boiling point and composition of the vapour given off from mixtures containing more water than the constant boiling mixture were determined under atmospheric pressure; up to 60 per cent. of perchloric acid, less than 1 per cent. of the latter is found in the vapour. Owing to decomposition at the ordinary pressure, the boiling points of mixtures containing less water than the constant boiling mixture had to be determined under reduced pressure. The pure acid boils at 16° under 18 mm. pressure with slight decomposition; the evolved vapour contains small amounts of the compounds Cl_2O_7 and ClO_2 , and a certain quantity of the monohydrate remains behind in the distilling flask (compare Roscoe, *loc. cit.*).

The density and viscosity curves of the system have been determined at 50° and partly at 20° ; both curves show distinct maxima. In the former case, the maximum corresponds approximately with the composition of the hydrate $\text{HClO}_4 \cdot \text{H}_2\text{O}$; in the viscosity curve, it lies between the mono- and the di-hydrate. The following values were obtained for the density of the pure acid: sp. gr. 1.7676 at $20^{\circ}/4^{\circ}$; 1.7098 at $50^{\circ}/4^{\circ}$.
G. S.

Bromine Fluoride, BrF_3 . PAUL LEBEAU (*Compt. rend.*, 1905, 141, 1018—1020. Compare Prideaux, *Proc.*, 1905, 21, 240).—Fluorine combines with bromine at 0° with incandescence forming *bromine trifluoride*, BrF_3 , a colourless liquid, solidifying in solid carbon dioxide to a crystalline mass melting at $4-5^{\circ}$, reacting violently with water, liberating oxygen, and forming hypobromous, hydrofluoric, and traces of bromic acids; a similar reaction occurs with solutions of the alkali carbonates. The solid compound reacts with incandescence with iodine below -10° to form iodine pentafluoride and bromine (compare Moissan, *Abstr.*, 1903, ii, 17), with sulphur to form fluorine and sulphur bromide, also with red phosphorus, arsenic, antimony, boron, or silicon; it reacts with carbon on gentle heating, attacks most of the metals and many of their compounds, and behaves like fluorine towards organic compounds.
M. A. W.

Occurrence of Fluorine in Mineral Waters of the Pyrenees and in Geysers of the Yellowstone Park. JOSÉ CASARES (*Zeit. anal. Chem.*, 1905, 44, 729—735).—The author has previously recorded the detection of fluorine in certain Galician mineral waters (*Abstr.*, 1896, ii, 42) and now gives the quantities of this element found in mineral waters from the Pyrenees. Ten samples of water were examined and yielded amounts of sodium fluoride varying from 0.0095 to 0.0301 gram per litre. Four samples of water from the Portuguese border contained from 0.0024 to 0.0212. Fluorine was also detected in the water from geysers in the Yellowstone Park District of North America.
W. P. S.

Ozone. ROBERT LUTHER (*Zeit. Elektrochem.*, 1905, 11, 832—835).—Ozone dissolves in 0.1*N* sulphuric acid in accordance with Henry's law; the ratio of the concentration in the liquid to that in the gas is 0.23 at 20° and 0.44 at 0° .

The *E.M.F.* of an iridium electrode immersed in a solution of ozone increases by 0.027 volt when the concentration of the ozone solution is increased tenfold. Luther and Inglis (Abstr., 1903, ii, 406) found the corresponding increase at a platinum electrode to be 0.054 volt. The reason of the difference is unknown. T. E.

Electrolytic Formation of Thiosulphates. MARIO G. LEVI and M. VOGHERA (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 433—443).—The authors have studied the formation of sodium thiosulphate by the electrolysis of a solution containing sodium sulphide and sodium sulphite, the electrodes being of smooth platinum. In some cases, the cathodic sulphide solution was separated from the sulphite solution by means of a Puckall porous diaphragm, whilst in others a diaphragm was not employed. The results show that, notwithstanding the vigorous anodic oxidation which occurs, the velocity of the reaction,

$\text{SO}_3 + \text{S} + 2\text{O} = \text{S}_2\text{O}_3$, is such as to allow of the formation of thio-sulphate in appreciable quantity. The anodic current density does not appear to have a great influence on the yield of thiosulphate, which is, however, diminished by raising or lowering the temperature excessively. The best yield was obtained with a diaphragm at 25°, although in the absence of a diaphragm the yield is, in general, increased. T. H. P.

Action of Dextrose on Selenious Acid. WILLIAM OECHSNER DE CONINCK and CHAUVENET (*Compt. rend.*, 1905, 141, 1234—1235).—When selenious acid is reduced by dextrose in aqueous solution, a colloidal form of selenium is obtained which cannot be separated by filtration. The solution, which appears green by transmitted and reddish-brown by reflected light, slowly deposits a red, amorphous variety of selenium, insoluble in carbon disulphide and not affected by light; but if the solution is boiled, the selenium is partially transformed into the black, microcrystalline variety (Gutbier, Abstr., 1902, ii, 652). M. A. W.

Atomic Weight of Tellurium. II. ALEXANDER GUTBIER (*Annalen*, 1905, 342, 266—282. Compare Abstr., 1904, ii, 254).—[With WALTER WAGENKNECHT.]—A new determination of the atomic weight of tellurium has been made, using a material which has been purified by a special method.

From the crude (95 per cent.) tellurium, the metal was separated by sulphur dioxide and dried at a low temperature. It was then distilled under reduced pressure in a combustion tube. The further purification was then carried out by two methods, by conversion into telluric acid or by conversion into the basic tellurium nitrate.

The tellurium was oxidised to telluric acid by chromic acid and the product crystallised ten times from water in platinum vessels. It was then converted into the dioxide, which dissolved in hydrochloric acid without evolution of chlorine. Finally the material purified by either method was precipitated from hydrochloric acid by hydrogen sulphide as a sulphide, TeS_2 , or a mixture in the proportion $\text{Te}:\text{S}_2$; from this, carbon disulphide extracted the major part of

the sulphur. The material, still containing 1.18 to 1.2 per cent. of sulphur, was now distilled under reduced pressure fourteen times. In the first twelve distillations, a small white residue was observed in the tube. Its chemical nature could not be discovered. The final product did not contain a detectable trace of sulphur or other impurity.

The tellurium dioxide was prepared for analysis by converting the metal into the basic nitrate, which was then carefully heated.

In one series of analyses, the dioxide mixed with silver and powdered quartz was reduced in a current of hydrogen. In five experiments, the value for the atomic weight lay between the limits 127.55—127.68 ($O = 16$).

In a second series of experiments, the dioxide was reduced by hydrazine hydrochloride at the ordinary temperature, the reduction being finally completed at a higher temperature. The tellurium was collected in a platinum crucible and dried in hydrogen. Three experiments gave the numbers 127.62, 127.67, and 127.55.

The mean of all the determinations gives the value 127.6; the new methods of purification have therefore not produced any change in the value of the atomic weight.

K. J. P. O.

Action of Nitrous Acid on Hydrazine. E. FRANCKE (*Ber.*, 1905, 38, 4102).—The decomposition of hydrazine by nitrous acid proceeds quantitatively according to the equation $N_2H_4 + HNO_2 = N_2O + NH_3 + H_2O$. The equation $N_2H_4, H_2SO_4 + 2NaNO_2 = N_2 + Na_2SO_4 + 2NOH + 2H_2O$, given by Girard and Saporta (*Abstr.*, 1904, ii, 678), could not be confirmed.

T. M. L.

Metallic Nitroso-compounds and Nitric Oxide. SIEGFRIED ZIMMERMANN (*Monatsh.*, 1905, 26, 1277—1294. Compare Chesneau, *Abstr.*, 1899, ii, 661; Kohlschütter and Kutscheroff, *Abstr.*, 1904, ii, 734).—Conductivity measurements were made with ferrous sulphate solutions before and after the passage of a current of nitric oxide for six hours. With an $N/16$ ferrous sulphate solution, the specific conductivity fell from 645.6 to 625.5, but with $N/32$, $N/64$, and $N/128$ solutions the specific conductivities rose from 377.0, 217.9, and 129.8 to 382.4, 229.4, and 152.3 respectively. Conductivity water, through which a current of nitric oxide is passed for 3, $4\frac{1}{2}$, $4\frac{3}{4}$, 5, 6, 15, 16, and 24 hours, has the specific conductivities $x_{NO} \times 10^5 = 16.85, 28.73, 29.45, 29.96, 36.24, 44.14, 44.61, \text{ and } 67.34$ respectively. In aqueous solution with $v = 497.375, 994.665, \text{ and } 1990.000$, nitric oxide has the specific conductivities $x_{NO} \times 10^5 = 17.18, 12.07, \text{ and } 10.13$, and the molecular conductivities $\mu_{NO} = 85.4, 120.39, \text{ and } 201.7$; it behaves therefore neither as a strong nor a weak acid. On deducting the specific conductivity $x_{NO} \times 10^5 = 36.2$ from the conductivities of the $N/16, N/32, N/64, \text{ and } N/128$ ferrous sulphate solutions, after the passage of nitric oxide for six hours, the specific conductivities are found to fall from $x \times 10^5 = 645.6, 377.0, 217.9, \text{ and } 129.8$ to 589.3, 346.2, 193.2, and 116.1, the molecular conductivities from $\mu = 103.30, 120.64, 139.46, \text{ and } 166.14$ to 94.29, 110.78, 123.65, and 148.61 respectively. The complex ferrous-nitric oxide ion has therefore a smaller velocity than the ferrous ion.

G. Y.

Dissociation of Nitric Acid. PETRU BOGDAN (*Zeit. Elektrochem.*, 1905, 11, 824—826).—From determinations of the coefficients of partition of nitric acid between ether and water, it is possible to draw conclusions as to the concentration of the undissociated molecules of nitric acid in the aqueous solution, since determinations of the boiling points of ethereal solutions of nitric acid show that the molecular weight of nitric acid dissolved in ether is normal. The results are calculated in the way described by Rothmund and Drucker (Abstr., 1904, ii, 231), and the conclusion is drawn that nitric acid follows Ostwald's law of dissociation, the dissociation constant lying between 3.0 and 3.5.

T. E.

Action of Gaseous Ammonia on Phosphorus Tribromide or Tri-iodide. CHARLES HUGOT (*Compt. rend.*, 1905, 141, 1235—1237. Compare Abstr., 1904, ii, 559).—By the action of ammonia on phosphorus tribromide at -70° in a special apparatus described previously (compare Abstr., 1901, ii, 18), *phosphoramidite*, $P(NH_2)_3$, is obtained together with ammonio-ammonium bromide, $NH_4Br \cdot 3NH_3$ (Troost, Abstr., 1881, 972). Phosphoramidite is an unstable yellow solid insoluble in ammonio-ammonium bromide; it begins to decompose at -25° into *phosphorimide*, $P_2(NH)_3$, and ammonia, and the change is complete in twenty-four hours at 0° . Phosphorimide is a brown solid decomposing on heating into ammonia, nitrogen, and phosphorus. When phosphorus tri-iodide replaces the tribromide in the above experiment, a similar reaction occurs at -65° , but the phosphoramidite is soluble in the ammonio-ammonium iodide.

M. A. W.

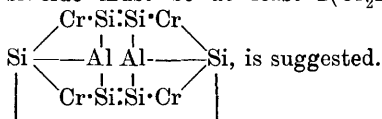
Electrolytic Reduction of Carbonic Acid. RICHARD EHRENFELD (*Ber.*, 1905, 38, 4138—4143. Compare Coehn and Jahn, Abstr., 1904, ii, 614).—Solutions of ammonium carbonate, obtained by dissolving commercial ammonium carbonate in one part of ammonium hydroxide of sp. gr. 0.910 and four parts of water, have been electrolysed in an apparatus in which the cathode and anode cells were separated by a porous diaphragm. Each experiment lasted twelve hours and was conducted at the ordinary temperature, the anode consisting of platinum foil. Ammonium formate was produced at the cathode when this consisted of amalgamated zinc and when a difference of potential of 5—10 volts and a current density of 0.01—0.08 ampere were employed. No formate could be detected (a) when iron, platinum, copper, lead, or nickel cathodes were used, (b) when the current density was less than 0.01 ampere, nor (c) when the solution was too dilute, for example, one-fifth the above concentration. Solutions of sodium carbonate or of carbonate and hydroxide do not yield formates under similar conditions.

The formation is not due to the presence of carbamate in the commercial carbonate, but is attributed to the presence of NH_4CO_3 anions in the concentrated solution.

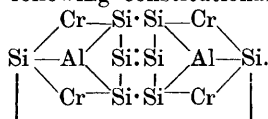
J. J. S.

Constitution of Silicides. II. Double Aluminium Silicides. WILHELM MANCHOT and A. KIESER (*Annalen*, 1905, 342, 356—363. Compare Abstr., 1905, ii, 165).—The empirical constitution of the

silicides of metals rarely throws any light on their constitution, but the amount of hydrogen evolved when they are decomposed with acids, generally hydrofluoric acid, occasionally affords a clue to the character of the linking in the silicide molecule. Aluminium chromium silicide, which was previously described (*loc. cit.*), readily dissolves in hydrofluoric acid with evolution of hydrogen. For each unit of valency of the metallic atoms in the silicide, two atoms of hydrogen should be produced in this reaction. The aluminium chromium silicide, Cr_2AlSi_3 , should yield fourteen atomic proportions of hydrogen, since here the chromium is bivalent as the solution of the silicide in hydrofluoric acid is blue. It is found, however, that nineteen atomic proportions of hydrogen are evolved. Since a molecule of the compound must yield an even number of atoms of hydrogen, the molecular formula of the silicide must be at least $2(\text{Cr}_2\text{AlSi}_3)$. The constitutional formula,



The silicide, Cr_2AlSi_4 , yields twenty-two atomic proportions of hydrogen, the increase of one atomic proportion of silicon increasing the hydrogen by three atomic proportions only. It is thought that the molecule must contain silicon atoms linked only with other atoms of silicon, a linking which is not broken by hydrofluoric acid. If the residue after treatment with hydrofluoric acid is subjected to the action of potassium hydroxide, which will break the linking of silicon with silicon, the proportion of hydrogen is increased to twenty-three atoms. The formula must be doubled in order to give an even number of hydrogen atoms. The following constitutional formula is suggested :



Simmonds' observations (Trans., 1903, 83, 1449 ; 1904, 85, 681) on the reduction products of lead silicate are not confirmed.

K. J. P. O.

Preparation and Purification of the Hydrogel of Silicic Acid. EDUARD JORDIS (*Zeit. Elektrochem.*, 1905, 11, 835—836. Compare Abstr., 1905, ii, 317).—By soaking the hydrogel of silicic acid in cold distilled water, the alkali chloride absorbed in it gradually diffuses out ; the washings leave less and less solid residue when they are evaporated until, finally, neither the washings nor the hydrogel gives the reactions of chlorine or alkali metal. If the hydrogel be now extracted with hot water, the washings give a strong reaction for both alkali metal and chlorine. The residue left on evaporating the washings does not diminish regularly, but rises and falls periodically. Much silica goes into solution, so that it appears as if a compound were dissolving as such.

T. E.

Two Lithium Mercuric Iodides. ANDRÉ G. DUBOIN (*Compt. rend.*, 1905, 141, 1015—1018).—The saturated solution of mercuric and lithium iodides having a sp. gr. 3.28 at 25.6° and $n = 1.783$ (Abstr., 1905, ii, 637) slowly deposits the *lithium mercuric iodide*, $2\text{LiI} \cdot \text{HgI}_2 \cdot 6\text{H}_2\text{O}$, in the form of long, flattened, deliquescent needles, having a sp. gr. 3.26 at 0°, readily soluble in methyl, ethyl, propyl, *iso*-propyl, *isobutyl*, amyl, or allyl alcohol, glycerol, acetaldehyde, acetone, formic or acetic acid, ethyl acetate, or oxalate, or ether, less soluble in nitrobenzene, ethylene bromide, or chloroform, insoluble in benzene or methyl iodide, and decomposed by water. The mother liquor from which the crystals have been removed yields at 8° a second *lithium mercuric iodide*, $2\text{LiI} \cdot \text{HgI}_2 \cdot 8\text{H}_2\text{O}$, in the form of large, soft, prismatic crystals, melting in the hand, having a sp. gr. 2.95 at 0°, closely resembling the first compound in solubility, but insoluble in ethylene bromide and almost so in nitrobenzene. M. A. W.

Decomposition of Mixtures of an Alkali Carbonate and an Alkaline Earth Carbonate under the Action of Heat in a Vacuum. PAUL LEBEAU (*Ann. Chim. Phys.*, 1905, [viii], 6, 433—441).—In addition to the decomposition of mixtures of calcium carbonate with an alkali carbonate already described (Abstr., 1905, ii, 561, 616), the effect of high temperatures on mixtures of lithium carbonate with strontium or barium carbonate has been examined; such mixtures are completely decomposed at 1150° to 1250°, the residue consisting of pure crystalline strontia or baryta respectively. M. A. W.

Separation of Silver from Silver Sulphide in the Presence of Mercury. F. WILLY HINRICHSSEN and TOSIO WATANABE (*Chem. Centr.*, 1905, ii, 1642—1644; from *Festschr. 70 Geburtstag Adolf Wüllner*, 214—216).—The conditions of equilibrium of systems consisting of silver sulphide, mercury, sodium chloride, and water, and the effect of replacing mercury by other metals, and sodium chloride by sulphuric acid or potassium cyanide, have been investigated with a view to elucidating the part played by mercury in the separation of silver from ores in the Patio and Kröhnke amalgamation processes.

The results of experiments in which mercury and silver sulphide were agitated together by means of a shaking thermostat showed that noticeable quantities of silver were removed from the sulphide when the proportion of mercury to silver sulphide was 11.5 to 1. The yield of silver increased with the duration of the experiment, but variation of the temperature from 15—40° appeared to have but little effect. When zinc amalgam was employed instead of mercury at 40°, the components mixed completely and the product formed a tough mass.

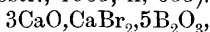
When a saturated solution of sodium chloride is shaken with mercury, no appreciable quantity of mercurous chloride is formed at the ordinary temperature or on boiling. The decomposition of silver sulphide by a solution of sodium chloride can only take place to a very limited extent on account of the very slight solubility of silver chloride. The conductivity of a solution of sodium chloride containing 64 grams per litre is not affected by the addition of silver sulphide, but when silver sulphide is added to a 20 per cent. solution of sodium chloride, the filtrate gives a precipitate of silver sulphide on addition of

ammonium sulphide. The action of mercury on silver sulphide is not so great at the ordinary temperature or at 40° when water is present as in its absence, but rise of temperature materially increases the yield of silver in the former case. When zinc amalgam is used instead of mercury, silver amalgam is not formed.

Experiments on the quaternary system: silver sulphide, mercury or zinc amalgam, sodium chloride, and water at 14° and 40° show that the decomposition is aided by rise of temperature or increase of the quantity of sodium chloride in solution. When a piece of silver foil, which has been coated with silver sulphide by immersing it in a warm solution of ammonium sulphide, and a rod of zinc are placed in a solution of sodium chloride and connected, silver is deposited on the latter and zinc sulphide is formed. Zinc amalgam together with mercury gives better yields than mercury alone, but at 40° the increase of the yield is only apparent in the case of more concentrated solutions of sodium chloride. Zinc amalgam does not attack silver sulphide to an appreciable extent in water, but decomposes forming zinc hydroxide. The *E.M.F.* of a zinc-silver sulphide couple in a 20 per cent. solution of sodium chloride is 0.965 volt at the ordinary temperature, whilst that of an iron-silver sulphide couple under similar conditions is 0.36—0.44 volt, hence iron cannot liberate silver from silver sulphide in a solution of sodium chloride. The decomposition of silver sulphide by mercury in the presence of sulphuric acid or potassium cyanide is considerably increased by the addition of a piece of iron, the effect being largely due to change of mechanical conditions, as glass produces a similar effect. When mercury is shaken with a solution of sodium chloride, small globules are formed, whilst with potassium cyanide the metal retains a continuous smooth surface. The decrease in the adhesion of mercury caused by water or a solution of salt probably accounts for the retarding influence of the water on the decomposition of silver sulphide by mercury. When zinc amalgam acts on silver sulphide in a solution of sodium chloride, the yield is improved by increasing the quantity of zinc, whilst the tendency of the amalgam to form globules becomes less; increase of the quantity of mercury produced a similar effect by enlarging the surface of contact. When iron acts on silver sulphide in a solution of potassium cyanide, the yield of silver is proportional to the concentration of the cyanide.

F. W. W.

Calcium Bromoborates. LÉON OUVRARD (*Compt. rend.*, 1905, 141, 1022—1024. Compare Abstr., 1905, ii, 635).—The salt,



obtained in a similar manner to the corresponding chlorine compound by fusing a mixture of boric anhydride (1 mol.) with calcium bromide (2 mols.), with or without the addition of lime (not more than 0.5 mol.), forms needles or prisms showing longitudinal extinction, almost insoluble in dilute acetic acid, but soluble in mineral acids; when the quantity of lime is increased to 1 mol., the compound, $3\text{CaO}, \text{CaBr}_2, 3\text{B}_2\text{O}_3$, is formed as transparent octahedra or arborescent, crystalline masses, feebly active towards polarised light, very sparingly soluble in water, but readily so in dilute acetic acid; if, however, the proportion of lime

is increased to 2 mols. or to 3 mols., crystals of calcium borate, $2\text{CaO}, \text{B}_2\text{O}_3$ or $3\text{CaO}, \text{B}_2\text{O}_3$, are obtained respectively.

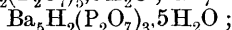
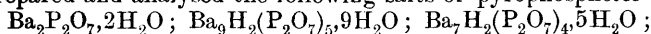
Attempts to prepare corresponding compounds containing iodine in place of chlorine or bromine were not successful (compare Ditte, *Abstr.*, 1883, 784). By fusing mixtures of boric anhydride (1 mol.) with calcium iodide (2 mols.) and varying proportions of lime, the borates $\text{CaO}, \text{B}_2\text{O}_3$, $2\text{CaO}, \text{B}_2\text{O}_3$, or $3\text{CaO}, \text{B}_2\text{O}_3$ were obtained, the last in the form of beautiful crystals when the proportion of lime reached 3 mols.

M. A. W.

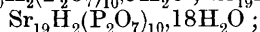
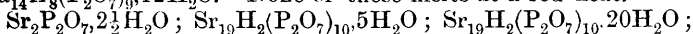
New Method of Preparing Barium. ANTOINE GUNTZ (*Compt. rend.*, 1905, 141, 1240—1241. Compare *Abstr.*, 1902, ii, 138).—Pure barium, containing 99.56 per cent. of the metal, can be obtained in small quantities by heating barium hydride (*Abstr.*, 1901, ii, 385) in a vacuum in an iron tube enclosed in a porcelain tube. The hydride begins to dissociate at 900° , and at 1200° the barium volatilises and is condensed in a polished steel tube cooled by cold water, in the form of a silver-white, crystalline metal having a sp. gr. 3.78, that of the hydride being 4.21.

M. A. W.

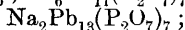
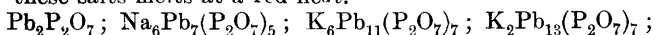
Pyrophosphates of Barium, Strontium, and Lead. C. N. PAHL (*Arkiv Kem. Min. Geol.*, 1905, 2, i, No. 6, 1—8).—The author has prepared and analysed the following salts of pyrophosphoric acid :



$\text{Ba}_{14}\text{H}_8(\text{P}_2\text{O}_7)_9, 12\text{H}_2\text{O}$. None of these melts at a red heat.



$\text{Sr}_9\text{H}_2(\text{P}_2\text{O}_7)_5, 12\text{H}_2\text{O}; \text{Sr}_9\text{H}_2(\text{P}_2\text{O}_7)_5, 8\text{H}_2\text{O}; \text{Sr}_3\text{H}_2(\text{P}_2\text{O}_7)_5, 3\text{H}_2\text{O}$. None of these salts melts at a red heat.

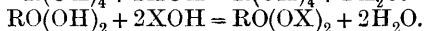
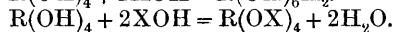


$\text{Pb}(\text{OH})_2, 3\text{Pb}_2\text{P}_2\text{O}_7, \text{H}_2\text{O}$, all of which melt readily and re-solidify in the crystalline form.

T. H. P.

Constitution of certain Plumbates. ITALO BELLUCCI and NICOLA PARRAVANO (*Gazzetta*, 1905, 35, ii, 500—509).—In the salt described as potassium metaplumbate, to which the formula $\text{K}_2\text{PbO}_3, 3\text{H}_2\text{O}$ is assigned, the water is present as water of constitution, so that the formula $\text{Pb}(\text{OH})_6\text{K}_2$ must be ascribed to this salt (compare *Abstr.*, 1905, ii, 395).

The three metals, platinum, tin, and lead, all form salts of the three types $\text{R}(\text{OH})_6\text{X}_2$, $\text{R}(\text{OX})_4$, and $\text{RO}(\text{OX})_2$, which may be regarded as derived either from the ortho-hydrate, $\text{R}(\text{OH})_4$, or from the meta-hydrate, $\text{RO}(\text{OH})_2$:



T. H. P.

New Analogies between Thallium and Aluminium. VALENTINO FORTINI (*Gazzetta*, 1905, 35, ii, 450—460).—The position of thallium in the third group of the periodic system of the elements is

perfectly justified by its very intimate relations with aluminium, evidenced by the following facts: (1) thallium sesquioxide can replace alumina in the alums; (2) like indium, thallium and probably also aluminium form, with the sulphates of the alkali metals, double sulphates crystallising with eight molecules of water. T. H. P.

Chemistry of the Rare Earths. GRÉGOIRE N. WYROUBOFF and AUGUSTE VERNEUIL (*Ann. Chim. Phys.*, 1905, [viii], 6, 441—507).—A *résumé* of work already published (Abstr., 1898, ii, 222, 339; 1899, ii, 105, 224, 423, 598; also Wyrouboff, Abstr., 1901, i, 7, 579; ii, 149, 604; 1902, ii, 565, 609). M. A. W.

Samarium Sulphates. CAMILLE MATIGNON (*Compt. rend.*, 1905, 141, 1230—1232).—*Samarium hydrogen sulphate*, $\text{Sm}(\text{HSO}_4)_3$ or $\text{Sm}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{SO}_4$, obtained by evaporating at 200° a sulphuric acid solution of the normal sulphate or by allowing the boiling solution to cool, forms thin needles, less soluble than the corresponding salts of praseodymium or neodymium (compare Abstr., 1902, ii, 325). The *basic samarium sulphate*, $(\text{SmO})_2\text{SO}_4$ or $\text{Sm}_2\text{O}_3 \cdot \text{SO}_3$, prepared by heating the normal sulphate at 1000° , is a pale yellow, amorphous powder, insoluble in water or in cold dilute sulphuric acid.

The atomic weight of samarium determined by the conversion of the normal into the basic sulphate is 150.6 ($\text{O} = 16$) (compare Urbain and Lacombe, Abstr., 1904, ii, 486). M. A. W.

Alloys of Aluminium and Antimony. GUSTAV TAMMANN (*Zeit. anorg. Chem.*, 1905, 48, 53—60. Compare Campbell and Matthews, Abstr., 1902, ii, 399).—It was shown by Gautier and by Campbell and Matthews (*loc. cit.*) that the melting-point curve of alloys of aluminium and antimony has two maxima at about 18 and 68 per cent. by weight of the former metal respectively, the first of which corresponds with the formula AlSb , whereas the second does not correspond with any simple formula; microscopic examination showed only the presence of the compound AlSb and its components. In the present paper, it is pointed out that if two metals enter into combination very slowly, the melting point curve may show a maximum at a point where no chemical compound exists, and its position will depend on how long the alloy has been heated.

In agreement with this, it is found that the compound AlSb is formed very slowly from its components. On heating the metals in equivalent proportion at 715° for one hundred minutes, only 1/10, and in thirty minutes at 1100° only 3/4, has entered into combination. If the above theory is true, there ought to be no second maximum if the alloy is kept at a high temperature sufficiently long for complete combination to take place, but this could not be tested in the present instance owing to the action of the fused alloy on the porcelain tubes used in the experiments. G. S.

"Temper" Carbon and Graphite in Iron. F. WÜST and C. GEIGER (*Chem. Centr.*, 1905, ii, 1642; from *Stahl u. Eisen*, 25, 1134—1139).—Experiments on two kinds of white iron have shown

that small quantities of "temper" carbon are formed even at comparatively low temperatures, the time required varying inversely with the temperature. The greater portion of this form of carbon is formed suddenly at a certain temperature which varies with the quality of the iron. Up to temperatures near the melting point, the quantity formed in this way is greater the higher the temperature, but by prolonged heating at the same temperature the quantity is only slightly increased, a state of equilibrium being attained. The speed of cooling has but little effect on the quantity of temper carbon. When once formed in cast iron, the quantity may be increased by reheating, the increase being greater the nearer the temperature to a certain fixed temperature. Temper carbon does not disappear when the iron is quenched. This form of carbon cannot be assumed to be present in the form of iron carbide, Fe_3C . It is not removed in a gaseous state by the action of pure dry hydrogen or nitrogen, and the process of tempering can only be effected by substances which can give up oxygen. Graphite may be eliminated in a gaseous form by carbon dioxide, hydrogen, or iron oxide.

E. W. W.

Physical and Chemical Properties of Iron Carbonyl. Sir JAMES DEWAR and HUMPHREY O. JONES (*Proc. Roy. Soc.*, 1905, 76 A, 558—577. Compare Abstr., 1903, ii, 485).—The yellow colour of iron carbonyl is characteristic of the pure substance and is not due to impurities. The best method of decomposing the substance consists in treating it with alcoholic potash in a sealed tube at 100° . The formula $\text{Fe}(\text{CO})_5$ has been confirmed by repeated analyses, and the following physical data have been determined: sp. gr. 1.4937 at $0^\circ/4^\circ$, 1.4565 at $21.1^\circ/4^\circ$, 1.4330 at $40.0^\circ/4^\circ$, 1.3825 at $60^\circ/4^\circ$; mean coefficient of expansion 0.00138 ; boiling point 102.5° under 760 mm. pressure; melting point -19.5° to -20° ; molecular volume at boiling point 149.6 , at freezing point 128 ; refractive index for sodium light 1.519 , for thallium light 1.528 at 22° ;

Vapour pressure at	-7°	0°	16.1°	18.4°	35°	57°	78°
	14.0	16.0	25.9	28.2	52.0	133.0	311.2 mm;

critical temperature, 285 — 288° , which agrees closely with the relationship $T = 0.66T_c$; critical density, 0.49 ; critical pressure, 29.6 atmospheres; latent heat of vaporisation, 39.45 cal., in agreement with the Trouton constant. Cryoscopic measurements of the molecular weight in benzene solution gave 197 and 194 (theory 198). In vapour form, the substance dissociates at higher temperatures. The dissociation is of the order of 1 per cent. at 13° , and is practically complete at 216° ; it increases with diminution of pressure and is much smaller in an atmosphere of carbon monoxide than in an inert gas. Compared with nickel carbonyl, the iron compound is much more stable, and dissociation takes place slowly.

In carbon tetrachloride solution, the halogens react with iron carbonyl to form carbon monoxide and the corresponding ferrous salts. In the case of chlorine, ferric chloride is formed almost completely when a large excess of the halogen is employed. The velocity of the change

diminishes very considerably from chlorine to iodine. Iodine monochloride and iodine trichloride in chloroform solution form carbon monoxide and ferrous chloride. Cyanogen gas has no action on pure iron carbonyl, and in alcoholic solution the reaction is very slow. Cyanogen iodide in chloroform solution forms ferrous cyanide and a little ferrous iodide. Gaseous hydrogen chloride and bromide are inactive, but hydrogen iodide decomposes the compound with the formation of ferrous iodide, carbon monoxide, and hydrogen. In chloroform solution, hydrogen chloride and bromide react slowly in a similar manner. These reactions are similar to those of nickel carbonyl, but take place much less rapidly. In contrast with this, iron carbonyl does not react with nitric oxide or with sulphur dissolved in carbon disulphide or xylene. Gaseous hydrogen sulphide has no action, but an alcoholic solution reacts slowly, forming ferrous sulphide, carbon monoxide, and hydrogen. Concentrated sulphuric acid and nitric acid dissolved in carbon tetrachloride or ether react rapidly, carbon monoxide and hydrogen being evolved. When heated with benzene and aluminium chloride in a sealed tube at 100° , benzaldehyde and anthracene are formed; in the cold, anthracene is not produced.

When exposed to sunlight, iron pentacarbonyl decomposes according to the equation $2\text{Fe}(\text{CO})_5 = \text{Fe}_2(\text{CO})_9 + \text{CO}$. The electric arc only induces the change slowly and a strong acetylene flame is almost without action. *Diferrononacarbonyl* consists of lustrous, orange, hexagonal plates which remain unchanged in dry air. To obtain it in a pure condition, the pentacarbonyl is dissolved in dry ether or light petroleum, the solution exposed to sunlight, and the crystals which separate dried over sulphuric acid and solid paraffin. It is practically insoluble in ether, light petroleum, or benzene, slightly soluble in methylal, ethyl alcohol, and acetone, and much more so in pyridine. It has a sp. gr. 2.085 at 18° . On heating, it decomposes at about 100° , according to the equation $2\text{Fe}_2(\text{CO})_9 = 3\text{Fe}(\text{CO})_5 + \text{Fe} + 3\text{CO}$, forming a green liquid. When heated with ether, light petroleum, or toluene, the change takes place at about 50° and the liquid becomes intensely green. These green solutions on exposure to light again deposit the solid carbonyl and become colourless.

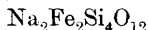
The decomposition of the pentacarbonyl in sunlight is not influenced by increasing the pressure to 125 atmospheres. On the other hand, if heated at 60 — 100° during the exposure, no decomposition takes place. When dissolved in ether, light petroleum, or amylene and exposed to sunlight at the temperature of liquid air, slow decomposition takes place. The reaction induced by light is slowly reversed in the dark, tubes containing pentacarbonyl which had been exposed to light becoming clear when left in the dark for several weeks.

Blue light is most active in effecting the above change, then follow green and yellow light, with red last. It takes place much more readily in ether, light petroleum, or alcohol than in benzene. When dissolved in nickel carbonyl, the decomposition by light is very slow, and a 10 per cent. solution does not deposit solid or evolve gas, even after several weeks' exposure to bright sunlight. To account for this, it is suggested that combination takes place, resulting in the formation

of a compound, $\text{FeNi}(\text{CO})_9$, which is not acted on by light. This view is in harmony with the fact that these solutions are much paler in colour than corresponding solutions of the pentacarbonyl in other solvents.
H. M. D.

Oxidation of Ferrous Chloride by Water with Evolution of Hydrogen. HEINRICH PRECHT (*Zeit. angew. Chem.*, 1905, 18, 1935—1936).—Further evidence to prove that explosive gases met with in the Stassfurt potash deposits consist of hydrogen formed by the oxidation of ferrous chloride by water. In solutions very rich in magnesium chloride, ferrous chloride is not oxidised. Should magnesium hydroxide, however, be present, ferrous hydroxide will be precipitated, and this will be oxidised gradually by water with liberation of hydrogen.
L. DE K.

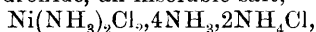
The Silicate $\text{Na}_2\text{Fe}_2\text{Si}_4\text{O}_{12}$. Z. WEYBERG (*Centr. Min.*, 1905, 717—719).—Following on his experiments with the aluminosilicates containing the group $\text{Na}_2\text{Al}_3\text{Si}_2\text{O}_8$, characteristic of the sodalite series (Abstr., 1905, ii, 89, 98), the author has attempted to prepare the corresponding iron compounds, but without success, there resulting usually spinels, hæmatite, or indefinite products. In one case, however, a definite crystallised product with the composition



and the form of small, yellow prisms was obtained; this was formed when a mixture of silicic acid, ferric hydroxide, and sodium carbonate in the proportions $2\text{SiO}_2 : \text{Fe}_2\text{O}_3 : \text{Na}_2\text{O}$ was fused with a large amount of sodium chloride.
L. J. S.

Cobalt and Nickel. H. COPAUX (*Ann. Chim. Phys.*, 1905, [viii], 6, 508—574).—In addition to a detailed account of work already published (compare Abstr., 1902, i, 586; 1903, i, 309, ii, 454; 1905, ii, 254), a description of *cobaltic selenate*, $\text{Co}_3(\text{SeO}_4)_3 \cdot 18\text{H}_2\text{O}$, is given; the salt, which is unstable, is prepared by electrolysing a solution of cobaltous selenate at -10° .
M. A. W.

Preparation of a Double Salt of Ammonio-nickel Chloride. HANS A. FRASCH (D.R.-P. 161119. Compare Abstr., 1904, ii, 128).—When an excess of an alkali chloride is added to an ammoniacal solution of nickel hydroxide, an insoluble salt,



is precipitated. The formation of the ammonium chloride may be represented in the following way: $\text{Ni}(\text{OH})_2 + 6\text{NH}_3 + x\text{NaCl} = \text{Ni}(\text{NH}_3)_2\text{Cl}_2 \cdot 4\text{NH}_3 + 2\text{NaOH} + (x-2)\text{NaCl}$; $\text{Ni}(\text{NH}_3)_2\text{Cl}_2 \cdot 4\text{NH}_3 + 2\text{H}_2\text{O} = \text{Ni}(\text{OH})_2 + 2\text{NH}_4\text{Cl} + 4\text{NH}_3$. In presence of an excess of alkali salt, the insoluble salt is precipitated. It resembles the salt formerly described, and may be used to separate nickel from other metals forming hydroxides soluble in ammonia.
C. H. D.

Nickelonickelic Oxide. HENRI BAUBIGNY (*Compt. rend.*, 1905, 141, 1232—1233).—Polemical, in reply to Bellucci and Clavari (Abstr., 1905, i, 823).
M. A. W.

Triammine Chromium Tetroxide. ERNST H. RIESENFELD [with WILLIAM A. KUTSCH and HERMAN OHL] (*Ber.*, 1905, 38, 4068—4074. Compare Riesenfeld, Wohlers, and Kutsch, *Abstr.*, 1905, ii, 461, 824, 825).—Contrary to Hofmann and Hiendlmaier's statement (*Abstr.*, 1905, ii, 716), the action of hydrogen peroxide on ammonium chromate, whether containing 2.5 per cent. of free ammonia or saturated with ammonia, leads to the formation of ammonium perchromate, $(\text{NH}_4)_3\text{CrO}_8$, unless insufficient peroxide is used or the temperature is allowed to rise above 0° , when a mixture of ammonium perchromate and Weide's triammine chromium tetroxide, $\text{CrO}_4 \cdot 3\text{NH}_3$ (*Abstr.*, 1898, ii, 28), or the latter alone, is obtained. When treated with 10 per cent. ammonia, ammonium perchromate changes immediately at 40° , but only slowly at the laboratory temperature, into Weide's compound, which separates in needles and rectangular and rhombic plates. The three forms have the sp. gr. 1.964 at 15.8° , and when examined crystallographically appear probably to be identical, and do not constitute two isomeric substances as stated by Hofmann and Hiendlmaier (*loc. cit.*). The action of dilute sulphuric acid on Weide's compound leads to the formation of chromium sulphate and hydrogen peroxide, but not of chromic acid; the amount of oxygen evolved varies from 3.54 equivalents with 1 per cent. to 2.24 equivalents with 20 per cent. acid. G. Y.

Atomic Weight of Bismuth. ALEXANDER GUTBIER (*Zeit. Elektrochem.*, 1905, 11, 831).—[With LOTHAR BIRCKENBACH.]—The oxidation of the metal to the oxide is the only trustworthy method of determining the atomic weight. Twelve experiments by this method gave $\text{Bi} = 208.02$, the extreme values being 207.88 and 208.22.

Bismuth oxide, in presence of metallic silver and quartz sand, is reduced to the metal by ammonia at 250° . The mean of the experiments by this method is $\text{Bi} = 208.03$, the extreme values being 207.92 and 208.17.

[With HANS MEHLER.]—Eight analyses of bismuth bromide, in which the bromine was determined by means of silver, gave $\text{Bi} = 208.05$, the extreme values being 207.89 and 208.24. T. E.

Distillation of Gold. Gold-copper and Gold-tin Alloys. A New Preparation of the Purple of Cassius. HENRI MOISSAN (*Compt. rend.*, 1905, 141, 977—983).—Gold can be readily distilled when heated in the electric furnace, and with a current of 500 amperes and 110 volts 13.3 per cent. of a 150 gram ingot of gold was volatilised in $6\frac{1}{2}$ minutes (compare Moissan, *Abstr.*, 1893, ii, 507; Schuller, *Abstr.*, 1904, ii, 109). The surface of the residual gold presents a blistered appearance and is covered in patches with a thin film of crystalline graphite, which was dissolved in the molten metal and expelled at the moment of solidification. The volatilised gold condenses on a copper cooler placed inside the furnace in the form of deep yellow, leafy crystals with a purple reflex, or in filaments (compare Margottet, *Ann. École Normal*, 1879, [ii], 8, 247; Liversidge, *Abstr.*, 1893, ii, 354; Ditte, *Abstr.*, 1900, ii, 549), or in brilliant yellow, cubical crystals, which contain small quantities of lime and graphite.

The boiling point of gold under atmospheric pressure, calculated from its boiling point in the vacuum of the cathode light, according to Krafft and Bergfeld (Abstr., 1905, ii, 244) is 2530° , and is higher than that of copper or tin; when, therefore, gold-copper or gold-tin alloys (compare Roberts-Austen, Abstr., 1901, ii, 25; Heycock and Neville, Trans., 1891, 59, 936; Maey, Abstr., 1901, ii, 655) are distilled in the electric furnace, the residual ingot is richer in gold than the original.

When the metallic vapours from a gold-tin alloy are allowed to escape into the air, the tin burns and a substance is obtained having the properties of the *purple of Cassius*, and containing tin dioxide, calcium oxide, and gold in varying proportions; and since similar purple colours are obtained by condensing the vapours evolved on distilling mixtures of gold with lime, alumina, magnesia, zirconia, or silica, Debray's view of the constitution of the purple of Cassius is probably correct (compare this Journ., 1873, 604; Abstr., 1885, 875).
M. A. W.

Sublimation of Platinum below its Melting Point. ANTOINE GUNTZ and HENRY BASSETT, jun. (*Bull. Soc. chim.*, 1905, [iii], 33, 1306—1308).—The authors have observed that there is slowly formed on the magnesia "brasque" of electric furnaces in the neighbourhood of the platinum electrodes a deposit of pure platinum. This occurs in crystals which may be either cubical or octahedral or a combination of these two forms.
T. A. H.

Solution of Platinum in Sulphuric Acid. MARCEL DELÉPINE (*Compt. rend.*, 1905, 141, 1013—1015. Compare this vol., ii, 24).—The solubility of platinum in pure sulphuric acid and in mixtures of sulphuric acid and potassium sulphate, measured by the loss in weight per hour of one square decimetre of platinum foil 10 to $20\ \mu$ thick, is 0.008 to 0.012 gram at 338° , the boiling point of sulphuric acid in a flask; 0.04 to 0.05 gram at 350 — 355° , the boiling point of a mixture of 50 grams of sulphuric acid and 10 grams of potassium sulphate; 0.12 to 0.13 gram at 365 — 370° , the boiling point of a mixture of 50 grams of sulphuric acid and 20 grams of potassium sulphate. The solubility of platinum in sulphuric acid is not to be attributed to the catalytic action of traces of nitrous compounds, as stated by Scheurer-Kestner (Abstr., 1876, i, 345; ii, 674; 1878, 650; 1880, 706), because platinum is dissolved to exactly the same extent in sulphuric acid containing less than $1/10,000,000$ of nitric acid as in acid containing $1/50,000$, $1/250,000$, $1/10,000$, or $1/1000$ nitric acid. Owing to the greater surface exposed, platinum sponge is more readily dissolved than platinum foil by sulphuric acid; the acid assumes a yellow colour, due to the presence of platinic sulphate, $\text{Pt}(\text{SO}_4)_2$, which is precipitated as potassium platinichloride on the addition of potassium chloride to the diluted solution.

Owing to the reducing action of ammonium sulphate, platinum foil does not appreciably lose in weight when boiled in sulphuric acid containing ammonium compounds (compare this vol., ii, 24, and Scheurer-Kestner, *loc. cit.*). The contrary result obtained by Conroy (Abstr., 1903, ii, 433) was probably due to the facts that his experiments were conducted at a lower temperature, 250° , and were of shorter duration.
M. A. W.

Oxidation of Palladium. LOTHAR WÖHLER (*Zeit. Elektrochem.*, 1905, 11, 836—844).—Palladium monoxide decomposes when heated in accordance with the equation $\text{PdO} \rightleftharpoons \text{Pd} + \text{O}$; the reaction is reversible. The dissociation tension of palladium monoxide is measured on a sample of oxide prepared by hydrolytic dissociation of the nitrate and dried in oxygen at 750—800°. A definite dissociation pressure curve is obtained by heating the oxide until equilibrium is attained at a series of temperatures, gradually rising. At the higher temperatures, both the oxide and the metal sinter; and if the temperature is lowered and then raised again, a new, higher dissociation tension is observed. A sample of palladium monoxide prepared by heating palladium sponge in oxygen at 700—830° gave a curve which up to about 750° agreed with the first curve, but at higher temperatures gave higher pressures. The author is inclined to ascribe this behaviour not to a mere retardation of the velocity of oxidation of palladium due to its diminished surface, but rather to a change in the energy of the oxide and metal alike, due to diminished surface. A change in the heat developed by the reaction changes the equilibrium constant (according to van't Hoff's equation), and in this case the heat development is very small. From the curve of dissociation tension, the author calculates the molecular heat of the reaction $\text{PdO} = \text{Pd} + \text{O}$ to be about -23.5 Cals. The dissociation pressure of palladium monoxide reaches 760 mm. at 877°. It is difficult to oxidise palladium completely by heating it in presence of oxygen owing to the sintering of the metal and consequent slow attack; palladium sponge is the best material; it should be heated in pure oxygen at temperatures rising slowly from 700° to 840°. Palladium dioxide in presence of oxygen at atmospheric pressure is incapable of existence above 200°; it decomposes thus: $\text{PdO}_2 = \text{PdO} + \text{O}$. The reverse reaction takes place too slowly to be observed. T. E.

Physiological Chemistry.

Chemical Methods by which the Eggs of the Mollusc *Lottia Gigantea* can be caused to become Mature. JACQUES LOEB (*Univ. Calif. Publ., Physiology*, 1905, 3, 1—8).—It is found that the eggs of the limpet *Lottia gigantea*, which could not be fertilised by sperm in normal or acidified sea-water, could be fertilised easily in alkaline sea-water. This is not due to an influence on the sperm, but on the egg-cell. The maturing effect is due to chemical, not physical action; this conclusion is reached from experiments on the influence of temperature, an increase in which accelerates the velocity of chemical reactions more rapidly than it modifies any physical quality. Oxygen is also necessary for maturation. The methods that cause artificial parthenogenesis must also incidentally cause the

maturation of the eggs. Treatment of the eggs with a fat solvent such as benzene also causes maturation.

W. D. H.

Resistance to Lack of Oxygen and a Method of Increasing it. WALES H. PACKARD (*Amer. J. Physiol.*, 1905, 15, 30—41).—By increasing the alkalinity of the blood of *Fundulus* by the injection of sodium hydrogen carbonate, its resistance to lack of oxygen is increased. Decreasing the alkalinity by the injection of acetic acid lessens the power of resistance. Increase of the amount of levulose in the blood has no such effect.

W. D. H.

Influence of Temperature on Vital Processes. RICHARD ABEGG (*Zeit. Elektrochem.*, 1905, 11, 823).—The rate of production of carbon dioxide by frogs is approximately doubled by an increase of temperature of 10° between 14° and 25°. The same is true of rabbits between 38·6° and 40·6° (compare Herzog, this vol., ii, 115).

T. E.

Assimilation of Carbon Dioxide by Chrysalides of Lepidoptera. MARIA (GRÄFIN) VON LINDEN (*Compt. rend.*, 1905, 141, 1258—1260. Compare Abstr., 1903, ii, 677; and Engelman, *ibid.*, 1883, 611).—When chrysalides are kept in pure air, the production of carbon dioxide is greater at night than in the day-time, the relations between oxygen absorbed and carbon dioxide exhaled, CO_2/O_2 , being respectively 0·76 and 0·664. In winter, production of carbon dioxide may cease altogether.

In an atmosphere containing carbon dioxide, there is often an absorption of carbon dioxide and elimination of oxygen. In 113 experiments in winter, carbon dioxide was absorbed 37 times and oxygen exhaled 4 times. In the spring (116 experiments), the numbers were 60 and 63 respectively. Assimilation occurred more frequently in the day-time than at night. Respiration is more vigorous in the night.

N. H. J. M.

Formation of Hæmoglobin in the Embryo. LOUIS HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1905, 141, 848—849).—The hæmatogen of the egg belongs to the class of paranucleins; on cleavage, like hæmoglobin, it yields a proteid and a pigment containing iron. It is believed to play a greater part in nutrition than that of an oxygen carrier, containing as it does a reserve of sulphur, phosphorus, calcium, and magnesium.

W. D. H.

Classification of Blood-corpuscles. G. H. SCOTT (*J. Path. Bact.*, 1906, 11, 64—83).—The colourless corpuscles are classified as follows:

(1) The finely granular eosinophile or neutrophile leucocyte. (2) The coarsely granular eosinophile leucocyte. (3) The basophile leucocyte. (4) The hyaline leucocyte. (5) The lymphocyte.

The first four originate from immature forms termed myelocytes in the red marrow. The lymphocyte is the lymph cell of adenoid tissue. The coloured corpuscles are classified into:

1. The megalocytes, or embryonic red corpuscles ; these are nucleated and originate from immature forms termed megaloblasts in the marrow. The free nuclei of these cells are sometimes found in the blood.

2. The normal red corpuscles, which originate in the marrow from immature nucleated normoblasts. The nucleus of the normoblast is not discharged, but is absorbed within the cell, hence the biconcave form of the red disc.

Neither myelocytes nor nucleated immature red corpuscles undergo further development into mature forms when once they have made their way into the circulating blood. They are foreign elements, are filtered out by the spleen, and are the cause of the splenic tumour in leucæmia.

Leucocytes do not grow larger as they become mature, but shrink in size. Lymphocytes do grow larger, and may thus be distinguished into immature and mature ; they do not grow into the other varieties of colourless corpuscles.

W. D. H.

Hæmolytic Receptors of the Red Corpuscles. ROBERT MUIR and ALEXANDER R. FERGUSON (*J. Path. Bact.*, 1906, 11, 84—94).—The receptors are shown to be comparatively stable substances ; they are not destroyed when the blood is laked, but remain attached to the stromata of the corpuscles. They do not pass through a porcelain filter when the lysis is produced by serum ; but when the laking is performed with water (a more disruptive agent) a small fraction passes through.

W. D. H.

Action of Ricin on Lecithin. O. PASCUCCI (*Beitr. chem. Physiol. Path.*, 1905, 7, 457).—Ricin has an agglutinating action on blood-corpuscles. The present preliminary statement relates to its action on three constituents of the stroma of the corpuscles, namely, lecithin, cholesterol, and cerebrin. If a lecithin emulsion is prepared with as little alcohol as possible and a large amount of physiological saline solution, and a few drops of ricin dissolved in the same salt solution are added, the lecithin is precipitated in flocculent form and can be filtered off. The filtrate produces hæmolysis in an emulsion of blood-corpuscles ; the stromata can then be filtered off and the hæmoglobin passes into the filtrate. The original purely agglutinating action of the ricin has thus been transformed into a hæmolytic action. This opens a possibility of studying the quantitative relations of agglutination by hæmolysis. Cholesterol and cerebrin have no such action. If excess of ricin is added to the lecithin emulsion, the precipitate disappears and the lecithin is again in suspension.

W. D. H.

Iodine-staining Granules of Leucocytes. S. H. HABERSHON (*J. Path. Bact.*, 1906, 11, 95—123).—The microscopic and other observations recorded lead to the conclusion that glycogen or an iodine-staining substance of similar nature has a more definite relation to the colourless blood-corpuscles than has hitherto been recognised, and that whether derived from the liver or not (a point which the experiments

leave open), it is taken up by these cells and conveyed by them to the tissues, where it is utilised for the purposes of nutrition.

W. D. H.

Physicochemical Investigation on the Action of Carbon Dioxide on Blood. A. VON KORÁNYI and J. BENEC (*Pflüger's Archiv*, 1905, 110, 513—532).—The following conclusions have been arrived at: 1. For a solution of blood serum, the value $Q(R - 1.3228)$ is constant (Q = volume of solution containing 1 unit vol. of pigs' blood serum and R = the refractive index of the solution). 2.

$$R_1 = \frac{RS + R_K(Q - S)}{Q},$$

where R_1 = refractive index of a mixture containing S c.c. of serum and $Q - S$ c.c. of sodium chloride solution, R = original refraction of the serum solution, and R_K = the refraction of the chloride solution.

3. Alterations in the electrical conductivity of serum solutions caused by slight alterations in concentration are mainly due to alterations in the concentration of the albumin, and only to a slight extent to other factors.

4. The refractive index of a serum is at a minimum when the blood is rich in oxygen and poor in carbon dioxide.

5. An increase in the amount of carbon dioxide present causes a rapid increase in the refraction, but at the same time a diminution of the electrical conductivity of the blood.

6. The conductivity, on the other hand, is not appreciably affected by the amount of gas present in the blood.

7. The viscosity of blood is at a maximum when richest in carbon dioxide. As the carbon dioxide is replaced by oxygen, the viscosity diminishes, reaches a minimum, and then increases again with the amount of oxygen.

8. The viscosity increases with the number of blood corpuscles present, and the larger the individual corpuscles the greater is their influence on the viscosity.

9. The addition of acid to blood produces the same effects on the refractive index as the presence of carbon dioxide, and the addition of alkali hydroxide solutions effects similar to those produced by the replacement of carbon dioxide by oxygen. The amount of alkali required to produce a minimum refraction increases with the amount of carbon dioxide present.

10. The difference between the original value of the refractive index of the serum-common salt mixture and the minimum value obtained by the addition of alkali hydroxide increases with the amount of carbon dioxide present in the blood and also with the number of corpuscles present.

J. J. S.

Hæmolysis in Vitro and in Vivo. OSKAR R. VON WUNSCHHEIM (*Arch. Hygiene*, 1905, 54, 185—296).—The hæmolysis produced by various toxins has been mainly studied *in vitro*; in the present research, a comparative study of what occurs in the living body is also made. Among the many facts detailed, the following are some of

the most important. In chronic *Staphylococcus* infection with multiple abscesses, even although many bacteria are present in the blood, there is no hæmolysis during life or in the blood after death, but in the acute stage of infection, whether the injection is made intravenously or intraperitoneally, hæmolysis occurs during life, as evidenced by hæmoglobinæmia, and in the shed blood this continues. In *Streptococcus* infection, the serum of freshly-drawn blood is free from hæmoglobin, but if some time elapses after death before the blood is collected, the serum is stained with hæmoglobin. After death from infection with *Bacillus anthracis*, there is always hæmolysis and intense hæmoglobinæmia, but the change in the red corpuscles mainly occurs in the last few hours of life. A large number of other pathogenic organisms were investigated with somewhat similar results, all of which point to the danger of drawing conclusions from experiments in test-tubes without making parallel investigations during life.

W. D. H.

Action of Precipitins. FRIEDRICH OBERMAYER and ERNST P. PICK (*Beitr. chem. Physiol. Path.*, 1905, 7, 455—456).—By means of the authors' refraction method, an estimate of the amount of proteid matter in the precipitate produced by the mixture of a normal and an immune serum can be formed. The amount is very small; this confirms previous estimations by weighing.

W. D. H.

Anti-immune Substances and Complementoids. The Action of Complement as Agglutinin. ROBERT MUIR and C. H. BROWNING (*J. Hygiene*, 1906, 6, 1—19, 20—22).—Complementoid is the term applied to the material into which complement is changed by the temperature necessary to destroy the toxic action of the complement. When a large amount is present, it interferes with the combination of complement. Anti-immune substances or anti-amboceptors are obtained in serum in immunity experiments. They were first described by Bordet. The present research deals with details of their action.

Agglutination is usually produced by a single substance, agglutinin, possessed of combining and agglutinating groups, but it can also result from the co-operation of two substances in a manner analogous to what is seen in hæmolysis and bacteriolysis.

W. D. H.

Agglutination of Bacteria. GEORGES DREYER and A. J. JEX-BLAKE (*J. Path. Bact.*, 1906, 11, 1—47).—In this research, the nature of the changes produced in the agglutinating serum and in the bacteria is studied, and the action of acids, alkalis, and other chemical and physical agents on agglutination is described in full.

W. D. H.

Identity of Pepsin and Chymosin (Rennin). W. SAWJALOFF (*Zeit. physiol. Chem.*, 1905, 46, 307—331).—Pawloff's contention that gastric juice contains only one ferment which has both a proteolytic and a milk-curdling action is confirmed, mainly on the ground of experiments on reaction-velocity. The occurrence of a milk-curdling ferment in the gastric juice of animals such as fishes, which

never take milk, and also in the vegetable kingdom, is therefore capable of an easy explanation.

Although the formation of plasteins may be regarded as due to the reversed action of pepsin, the formation of casein from caseinogen does not come under that head. The latter is regarded merely as a masked stage in proteid digestion.

W. D. H.

Behaviour of Different Polypeptides towards Pancreas and Stomachic Juices. EMIL FISCHER and EMIL ABDERHALDEN (*Zeit. physiol. Chem.*, 1905, 46, 52—82. Compare Abstr., 1903, i, 694, 800; 1904, i, 867, 890, 917; 1905, i, 121, 122; ii, 333).—The list given in Abstr., 1905, ii, 333, has been extended by an examination of the following polypeptides:

Hydrolysed.	Not hydrolysed.
Alanylglycine.	Glycylalanine.
Alanylalanine.	Alanyl-leucine B.
Alanyl-leucine A.	Leucylalanine.
Leucylisoserine A.	Leucylglycine.
Alanylglycylglycine.	Leucyl-leucine.
Leucylglycylglycine.	Aminobutyrylglycine.
Glycyl-leucylalanine.	Aminobutyrylamino-
	butyric acids A and B.
	Aminoisovalerylglycine.
	Dileucylglycylglycine.

The following points are discussed: (1) Influence of structure. (2) Influence of the different amino-acids. (3) Influence of configuration. (4) The effect of the number of aminoacyl groups present. (5) Condition of the ferment. With respect to the last factor, it is shown that fresh pancreas juice obtained from a Pawloff fistula has not always the same action as commercial trypsin or pancreatin.

Glycyl-*L*-tyrosine, dialanylecystine, leucylalanine, leucylglycine, and leucyl-leucine are not fermented by the juices of the stomach.

J. J. S.

Pancreatic Juice rendered active by Calcium Salts. C. DELEZENNE (*Compt. rend.*, 1905, 141, 781—784).—When small amounts of a calcium salt (chloride, iodide, nitrate, or acetate) are added to pancreatic juice, the latter acquires the power of digesting albumins. The soluble calcium salts may be removed by dialysis, in presence of sodium chloride, without loss of activity, and addition of an excess of sodium fluoride to the dialysed juice has no effect.

All preparations are not rendered equally active by the same amount of calcium salt, owing to the varying amounts of alkali salts, especially sodium carbonate. Most of the calcium salt added is precipitated as carbonate or phosphate.

When pancreatic juice is filtered through collodion, it is no longer rendered active by calcium salts. It is suggested, with all reserve, that the substance retained by collodion may be a mother-substance of

kinase and that calcium salts transform it into a ferment in a manner more or less analogous to the production of the fibrin ferment.

N. H. J. M.

Activation of Pancreatic Juice by Salts. Specificity of Calcium. C. DELEZENNE (*Compt. rend.*, 1905, 141, 914—916).—Quite small quantities of calcium chloride increase the activity of pancreatic juice. The salt neutralises the carbonates and phosphates of the juice, and what is left over is the activating agent. Chlorides of strontium, barium, and magnesium are not capable of acting in the same way, or their action is extremely small.

W. D. H.

Changes of Refractive Properties of Glucosides and Proteids produced by Ferments, Acids, and Bacteria. FRIEDRICH OBERMAYER and ERNST P. PICK (*Beitr. chem. Physiol. Path.*, 1905, 7, 331—380).—The action of emulsin on amygdalin or salicin, of ptyalin on dextrin, and of acids on phloridzin produces no change in the refraction as measured by Pulfrich's refractometer. The sum of the action of the cleavage products is therefore equal to that of the intact molecules. The same is true for the peptic digestion of various proteids. After tryptic digestion, there is an increase of the refraction of from 5 to 7 in the fourth decimal place. From this, the conclusion is drawn that pepsin produces only a loosening of various complexes, whereas the action of trypsin is to cause a deeper "constitutional" change. The action of acids on proteids if it goes beyond the acid albumin stage resembles that of trypsin. Bacterial decomposition in the cases investigated lowers the refraction.

W. D. H.

Influence of Salts intimately united with Albuminous Material and with Enzymes on Proteolysis. G. MALFITANO (*Compt. rend.*, 1905, 141, 912—914).—The protease of anthrax rapidly liquefies gelatin, but has no effect on coagulated white of egg. If, however, the latter is previously boiled in physiological salt solution, it is rapidly dissolved by the protease. Boiling with a solution of calcium chloride of equivalent strength renders the egg-white refractory not only to the protease but also to activated pancreatic juice. Mixtures of kinase and pancreatic juice poor in the latter constituent behave exactly like the anthrax protease.

W. D. H.

Digestion in Elasmobranch Fishes. M. X. SULLIVAN (*Amer. J. Physiol.*, 1905, 15, 42—45).—These fishes (dogfish, sharks, &c.) swallow without mastication; there are no glands in the mouth region. Extracts of the mucous membrane of mouth and gullet have no digestive action. The cardiac sac of the stomach secretes pepsin-hydrochloric acid. The pyloric tube has no digestive action. The same is true for the middle intestine, spiral valve, and rectal gland. The action of the pancreatic juice varies a good deal; the juice is activated by bile and by splenic extracts, but not by intestinal extracts. Although the gastric juice, in virtue of its relatively high percentage of acid, dissolves out the calcareous salts from the carapace of crabs and lobsters swallowed, there is no true digestion of chitin; the chitinous mass is triturated and finally excreted by the anal orifice.

W. D. H.

Diastatic Hydrolysis of Xylan. GASTON SEILLIÈRE (*Compt. rend.*, 1905, 141, 1048—1050).—Many non-carnivorous molluscs and some insect larvæ contain a diastase (xylanase) which converts xylan into xylose (compare Biedermann and Moritz, *Pflüger's Archiv*, 1898, 73, 236).
N. H. J. M.

Morphogenetic Reaction of the Alimentary Canal of the Frog's Larva on Muscle Proteids of different classes of Animals. EDWARD BABÁK (*Beitr. chem. Physiol. Path.*, 1905, 7, 323—330).—If tadpoles are fed on vegetable food, the length of their alimentary canal becomes much greater than when fed on meat. The kind of flesh makes, however, a considerable difference. The following numbers giving the relative lengths of the canal are averages obtained from hundreds of measurements: fed on frog's flesh, 6.6; on fish, 6.6; on horseflesh, 6.6; on mussels, 5.9; on crab meat, 7.6; on vegetable proteid, 8.3. There are chemical differences between the muscle proteids of vertebrate animals, but these seem to be insufficient to provoke a morphogenetic reaction. The greater difficulty in digestion of vegetable proteid calls forth greater digestive activity, and so a growth in the secreting surface; crab meat seems to be nearly as difficult to digest, but mussels much easier. The amount of fæces varies with the difficulty of digestion.
W. D. H.

Absorption of Lecithin in the Intestine. B. SLOWTZOFF (*Beitr. chem. Physiol. Path.*, 1905, 7, 508—513).—A part of the lecithin in food is discoverable in the lymph. The greater part is saponified by the steapsin of pancreatic juice. A further decomposition of choline does not occur with fresh lecithin preparations. Lecith-albumins are affected by pepsin-hydrochloric acid. In the acid albumin which is first formed, lecithin appears to be still united with albumin, and is absorbed as such when administered by the rectum.
W. D. H.

Influence of High Altitudes on General Nutrition. H. GUILLEMARD and R. MOOG (*Compt. rend.*, 1905, 141, 843—846).—From the examination of the urine, the conclusion is drawn that residence at great altitudes diminishes oxidation and diuresis and causes retention of fixed elements. This is most marked from the fourth to the eighth day after the beginning of the experiment; following that, a return to the normal slowly sets in.
W. D. H.

Influence of Diet on Growth and Nutrition. CHALMERS WATSON and ANDREW HUNTER (*Proc. Physiol. Soc.*, 1905, xiii; *J. Physiol.*, 33).—The experiments were made on rats; in these animals, a meat diet is injurious and causes loss of weight, stunting of growth, and early death. Although there is great similarity chemically between porridge and bread and milk, the former is injurious. In the case of animals deprived of their ovaries, the minimum proteid requirement is less than in normal females.
W. D. H.

The Effect of Abundant Proteid Food on Metabolism. MAX SCHREUER (*Pflüger's Archiv*, 1905, 110, 227—253).—The relationships

between respiratory exchanges and the proteid in the nutriment are compared in experiments on dogs. The increased consumption of oxygen and consequent increase of cell activity which occurs is not a lasting effect. W. D. H.

Considerations on Proteid Diet with reference to the Various Forms of Nitrogen it contains. LEWELLYS F. BARKER and B. A. COHNE (*J. Biol. Chem. New York*, 1906, 1, 229—238).—It is well known that certain articles of diet will “agree” and others “disagree” with people. On the supposition that this may be due to the distribution of the nitrogen, determinations of amide nitrogen, melanoidin nitrogen, diamino-nitrogen, and monoamino-nitrogen were made in various foods (veal cutlets, pork chops, sirloin, chicken, fish, &c. &c.) and the results given in tables. The differences are very striking, but their ultimate valuation is for the future. W. D. H.

Nuclein-metabolism and the Ferments concerned in Man and Animals. ALFRED SCHITTENHELM (*Zeit. physiol. Chem.*, 1905, 46, 354—370).—From experiments on autolysis of the spleen, it is shown that differences exist in various animals. In the spleen of the ox and horse, uric acid is formed, but not in that of man, dog, or pig. There are also small quantitative differences in the amount of amino-purines changed into oxypurines. W. D. H.

Feeding with Artificial Nutriment. W. FALTA and C. T. NOEGGERATH (*Beitr. chem. Physiol. Path.*, 1905, 7, 313—322).—Rats were fed on various purified proteids, starch and sugar, and fat, with the addition of salts, water, and, in some cases, of lecithin, cholesterol, and sodium nucleate, all obtained as pure as possible. In all cases, weight was rapidly lost, and death ensued usually after about 60 or 70 days. W. D. H.

Pituitary Feeding. WILLIAM H. THOMPSON and H. M. JOHNSTON (*J. Physiol.*, 1905, 33, 189—197).—Pituitary substance (whole gland dried at 45—50°) stimulates metabolism in the dog, as shown by the output of total nitrogen, urea, and phosphates (to a less degree) in the urine. The body-weight declines. The effects do not subside immediately when the pituitary feeding ceases. They are more pronounced when gland substance from a young animal is given. W. D. H.

Metabolism in Cretins. W. SCHOLZ (*Chem. Centr.*, 1905, ii, 1546; from *Zeit. exper. Path. Ther.*, 2, 271—384).—In cretins not treated by thyroid feeding, the secretion of urine is small, and there is retention of proteids and salts. The excretion of uric acid, creatinine, phosphate, and sodium chloride is especially small. The amounts of urea, xanthine bases, ammonia, and sulphates are normal. The excretion of alkaline earths in young cretins is increased. This is similar to what occurs in myxœdema. By feeding on thyroid, diuresis is produced, and the nitrogen output increased. The body-weight sinks, mainly on account of increased metabolism in non-nitrogenous material. The urea output is but little affected; in older cretins, the uric acid

excreted rises; in young cretins, this is preceded by a fall. The excretion of alkaline earths (especially calcium) is lessened, but the amount of phosphates in the urine is not much altered. There is a great rise in the acidity of the urine, especially in young cretins. The influence of the thyroid treatment is compared with that of other glands with an internal secretion, such as the ovaries. There is no agreement in the actions.

W. D. H.

Revival of the Excised Mammalian Heart by Perfusion with Oil. TORALD SOLLMAN (*Amer. J. Physiol.*, 1906, 15, 121—126).—The excised mammalian heart can be made to beat for a short time by perfusion with indifferent liquids such as mercury or oil; with mercury, vitality is soon lost; with oil, the beats cease after about half an hour. The conclusion drawn is that the mammalian heart-beat is the consequence of a stimulus initiated by the distension of the coronary vessels under pressure; it is, however, admitted that such an explanation will not hold for the hearts of cold-blooded animals which have no coronary vessels, and beat in solutions without pressure. If the explanation given for the mammal's heart is correct, the stimulation can be conceived more readily as originating in nervous than in muscular structures, and so the experiments favour the neurogenic theory of the origin of the mammalian cardiac contraction.

W. D. H.

Survival of the Excised Mammalian Heart. FRANK S. LOCKE and OTTO ROSENHEIM (*Zentr. Physiol.*, 1905, 19, 737—739).—A remarkable instance of prolonged survival of the excised heart of an adult rabbit is recorded. The perfusion fluid employed was Locke's (that is, Ringer's solution containing dextrose and saturated with oxygen at atmospheric pressure). During the nights and over Sunday perfusion was stopped and the heart remained quiescent. But whenever, during the course of four days, perfusion was recommenced, the heart resumed regular rhythmic contractions.

W. D. H.

Action of Saline Solutions on the Vitality of Blood-vessels. ROBERT A. HATCHER (*Amer. J. Physiol.*, 1906, 15, 144—147).—Experiments on the excised dog's kidney enclosed within an oncometer and perfused with various saline solutions show that after perfusion with a 0.9 per cent. solution of pure sodium chloride the vessels show no reaction to adrenaline after three hours' perfusion, and after ten to twenty-four hours' perfusion only a slight reaction occurs when a solution of oxyhæmoglobin is substituted for the saline solution. If Ringer's solution is used instead of the pure saline, these times are lengthened. If Locke's solution is employed (that is, Ringer's solution containing 1 per cent. of dextrose), the times are greatly lengthened; for instance, a reaction to adrenaline is obtained twenty to twenty-seven hours after the beginning of the perfusion.

W. D. H.

The Secretory Function of the Parotid in Man. EDUARD VON ZEBROWSKI (*Pflüger's Archiv*, 1905, 110, 105—173).—Changes in the

parotid secretion are due to changes in the stimulation of the buccal mucous membrane. The quantity of the stimulating material influences mainly the rapidity of secretion. The rise in rapidity is nearly proportional to the square root of the amount of stimulating substance. The intensity of the stimulus influences the rapidity and also the composition of the secretion. Chewing has an important effect. One-sided chewing influences mainly the gland on the same side. The alkalinity of the saliva is proportional to the amount of ash. The ash increases with rapidity of secretion. The digestive power of, and amount of oxydase in, the saliva are proportional to the amount of organic material it contains. The alkalinity of the saliva favours the digestion of starch.

W. D. H.

Action of Alkaloids on the Iris. HUGH K. ANDERSON (*J. Physiol.*, 1905, 33, 414—438. Compare Abstr., 1905, ii, 546).—After section of the third nerve, pilocarpine constricts the paralysed pupil more than the control, but physostigmine constricts it less. Both, however, constrict it for a longer time. After degenerative section of the short ciliary nerves, physostigmine has no effect, but pilocarpine constricts the pupil markedly. The former drug acts, therefore, on the nerve-ending, but pilocarpine on the muscle itself. After imperfect regeneration of the third nerve, physostigmine restores the light reflex, but pilocarpine does not. The impulses imperfectly transmitted by the regenerating fibres are blocked chiefly in the ciliary nerve-endings. Some months after removal of the ciliary ganglion, the denervated sphincter begins to respond again to physostigmine, but the exact nature of the regeneration to which this is due is uncertain; a second section of the ciliary nerves causes it to disappear again.

W. D. H.

Action of Dilute Solutions on Living Cells. THOMAS BOKORNY (*Pflüger's Archiv*, 1905, 110, 174—226).—Further research on the action of dilute solutions of metallic and other poisons, on the lines of the author's previous work (compare Abstr., 1905, ii, 476, 752), is given in detail. A tabular summary gives the main conclusions.

W. D. H.

Physiology of Cell Division. I. RALPH S. LILLIE (*Amer. J. Physiol.*, 1905, 15, 46—84).—The arrangement of colloid aggregates in the cell, especially the chromosomes, during mitosis indicates that mutual electrostatic attractions and repulsions play an important part in determining their positions and movements. By the use of floating magnetised needles, many of the mitotic figures can be simulated.

W. D. H.

Validity of Pflüger's Law for Paramœcium. FRANK W. BANCROFT (*Univ. Calif. Publ. Physiology*, 1905, 2, 193—215).—Certain physiologists, including Verworn, have stated that Pflüger's law as formulated for vertebrate muscle and nerve does not hold for certain invertebrate structures such as *Paramœcium*, and that excitation occurs mainly at the anode when a constant current is passed through the animal. The present paper shows how this mistake arose, and draws

the following conclusions: the cilia in the unstimulated *Paramœcium* are either at rest or striking backwards, thus producing a movement of the animal forwards. When stimulated, the principal feature is a reversal of the stroke, and of the movement of the animal. Adopting the reversal of the cilia as the criterion for stimulation, Pflüger's law holds for the stimulation of the cilia, for on making, and during the flow of, the current, the cathodal, and only the cathodal, cilia reverse, and on breaking the current the anodal cilia reverse. W. D. H.

Reactions of Infusoria to Chemical and Osmotic Stimuli. T. BRAILSFORD ROBERTSON (*J. Biol. Chem. New York*, 1906, 1, 185—202).—Experiments with *Paramecia* are described in which various solutions of electrolytes and non-electrolytes were employed and the movements of the animals noted. W. D. H.

Action of Anæsthetics and Narcotics. ORVILLE H. BROWN (*Amer. J. Physiol.*, 1905, 15, 85—97).—Anæsthetics and narcotics at certain concentrations cause liquefaction of starfish eggs in proportion to their narcotic power. Anæsthesia is possibly the result of an inhibition by the compounds formed on the enzyme actions of the cells. Mathews' idea that they produce their results by their influence on the respiratory elements (the bivalent carbon compounds) of the cell is considered tenable. W. D. H.

Diffusion in Jellies. KURT MEYER (*Beitr. chem. Physiol. Path.*, 1905, 7, 393—410).—Gelatin was dissolved in water, and the solution allowed to gelatinise in test-tubes; a solution of sodium chloride was placed on the surface of the jelly, and the depth to which it penetrated the cylinder of jelly determined at the end of a given time. It was found that the rate of diffusion diminished with the concentration of the gelatin. The bearing of this on physiological phenomena is pointed out. In cells there are colloidal materials of different concentrations, and in substances like cartilage the concentration is high. The presence of cell membranes denser than the cell contents must also influence the rate of diffusion. Experiments with other sodium salts led to corresponding results. W. D. H.

Formation of Acetone [in the Body]. GIUSEPPE SATTA (*Beitr. chem. Physiol. Path.*, 1905, 7, 458. Compare *Abstr.*, 1904, ii, 829).—Polemical against Waldvogel (*Abstr.*, 1905, ii, 735). W. D. H.

Oxidation of Amino-acids with the Production of Substances of Biological Importance. HENRY D. DAKIN (*J. Biol. Chem. New York*, 1906, 1, 171—176).—The formation of a carbohydrate from an amino-acid takes place during life, but the chemistry of the change is difficult to explain. Enzymes are present in the liver which remove ammonia from amino-acids (Lang); it is also probable that carbon dioxide is readily removed from their carboxyl group by enzyme activity, as in the transformation of ornithine into tetramethylenediamine. If ammonia and carbon dioxide are removed from an amino-acid, an alkyl group rich in carbon is left

which might be further transformed into carbohydrate, or into carbon dioxide and water.

Accordingly a method was selected which closely approximates to biochemical reactions, namely, Fenton's method of oxidation by means of hydrogen peroxide and a trace of a catalyst such as ferrous sulphate. At present, experiments have been made with glycine, alanine, and leucine. All of these may be represented by the formula $\text{NH}_2\cdot\text{CHR}\cdot\text{CO}_2\text{H}$, where R is either a hydrogen atom (as in glycine) or a methyl or isobutyl group (as in alanine and leucine respectively). On oxidation, all are readily resolved at the ordinary temperature into carbon dioxide, ammonia, and an aldehyde. In the case of glycine, formaldehyde is produced, the substance no doubt which is produced photosynthetically in plant life and is the forerunner of carbohydrate. The conversion of this substance into reducing sugars has already been accomplished in the laboratory by Butleroff and Fischer. Glycine given to animals without a pancreas increases the sugar output (Emden and Salomon). In the oxidation of glycine, formic and glyoxylic acids are formed at the same time, and this accounts for the small yield of aldehyde as compared with the yield from alanine and leucine. The formation of glyoxylic acid is not without interest, as this acid occurs in unripe fruit, and on ripening is converted into sugar.

In similar fashion, alanine yields acetaldehyde and acetic acid (but not pyruvic acid, the product corresponding with glyoxylic acid), whilst leucine yields isovaleraldehyde and isovaleric acid.

The oxidation of glycine is peculiar in that small quantities of oximinacetic acid and formaldoxime are formed. Their formation will explain the production of hydrogen cyanide from glycine by oxidation with nitric acid, which was observed by Plimmer. W. D. H.

The Distribution of Salicylic Acid in Normal and Infected Animals. SAMUEL BONDI and MARTIN JACOBY (*Beitr. chem. Physiol. Path.*, 1905, 7, 514—526).—If salicylic acid, or one of its salts, is administered to animals, the greater part of it is subsequently found in the blood; the skeletal tissues, in contradistinction to the muscles, are also rich in it. Animals infected with *Staphylococcus* excrete it more slowly than normal animals. In the blood, the drug appears to be mainly held by the red corpuscles. W. D. H.

Organ-proteid. JULIUS POHL (*Beitr. chem. Physiol. Path.*, 1905, 7, 381—392).—In order to study immunity phenomena in organs and tissues on the lines on which they have already been worked out in relation to the blood, it is necessary to have some knowledge of the characters of the proteids in organs. The present investigation relates to the liver and to the globulin which is the main proteid obtainable from that organ. It is not identical with fibrinogen or with myosin. Some attention is paid to its low coagulation temperature; admixture with blood-serum raises the coagulation point, and the presence of blood in the tissues is believed to prevent coagulation, which might otherwise occur at body temperature.

W. D. H.

Oxidation of Organic Substances by Ferrous Sulphate in the Presence of Animal Extracts. FR. BATTELLI and M^{lle}. L. STERN (*Compt. rend.*, 1905, 141, 916—918).—Ferrous sulphate behaves like anticatalase in relation to catalase. It is well known that this salt in presence of hydrogen peroxide exerts an energetic oxidising action. In addition to what is already known, lactic, acetic, and formic acids are in the list of substances thus decomposable with the formation of carbon dioxide. Without hydrogen peroxide, ferrous sulphate has no appreciable action.

Some observers have advanced the view that oxidation in animal tissues depends on the formation of peroxides, but the hypothesis has received no experimental proof. If, however, they are present they should be activated by ferrous sulphate. The present experiments with muscle extracts show that this is so, but the quantity of carbon dioxide liberated is variable. The variation appears to depend mainly on the freshness of the muscles. Twelve hours after death, the experiments are negative; the substance which ferrous sulphate activates is either rapidly destroyed or else other *post mortem* products hinder the action. The action goes best when a stream of air is passed through the mixture. Without oxygen, the action does not occur. These facts fit in with the hypothesis that peroxides exist in the muscles and are being continually reconstituted by absorption of oxygen. In the living organism, the ferrous sulphate is represented by anticatalase, which would thus play the part of a peroxydase.

W. D. H.

Moderating Action of Catalase on Oxidations produced by Extracts of Animal Tissues. FR. BATTELLI and M^{lle}. L. STERN (*Compt. rend.*, 1905, 141, 1044—1046).—Catalase diminishes the oxidations produced by ferrous sulphate in presence of an emulsion of animal tissues. This lends support to the view that hydrogen peroxide is formed in animal tissues, and it is suggested that the rôle of catalase may be to prevent excessive oxidation of organic substances.

N. H. J. M.

Cutaneous Excretion of Nitrogenous Substances. FRANCIS G. BENEDICT (*J. Biol. Chem. New York*, 1906, 1, 263—270).—The amount of nitrogen-containing material excreted through the skin is markedly increased by muscular labour; at rest, it averages in man 0.071 gram *per diem*; during work, it rises to 0.2 gram per hour. The more severe the work, the greater is the increase.

In accurate metabolism work, it will be necessary to recognise this almost unconsidered channel of nitrogen excretion.

W. D. H.

Ureter Pressure. V. E. HENDERSON (*J. Physiol.*, 1905, 33, 175—188).—The ureter pressure depends on and varies with the blood pressure, and is not a secretion pressure properly so-called. The minimum difference between ureter pressure and blood pressure will vary first with the rate of urinary production, and secondly with the proteid constitution of the plasma; hence the explanation given by Starling of the dimensions of this minimal difference and of the

absence of urinary flow with low blood pressure is probably correct. Reabsorption of water and of slightly diffusible substances may take place in the renal tubules.

W. D. H.

Amino-acids in Normal Urine. GUSTAV EMBDEN and HEINRICH REESE (*Beitr. chem. Physiol. Path.*, 1905, 7, 411—424).—By means of β -naphthalenesulphonic chloride, it is possible to obtain certain compounds of amino-acids from normal urine provided it is kept alkaline. The glycine compound is obtainable even although the urine has been previously freed from hippuric acid; small quantities of the alanine compound were also obtained. Whether these acids are free in the urine or in the form of a peptide is unsettled.

W. D. H.

Excretion of Creatinine. WALDEMAR KOCH (*Amer. J. Physiol.*, 1905, 15, 1—14. Compare Abstr., 1905, ii, 182).—Creatinine is excreted with remarkable constancy by the dog as well as by man. The excretion per kilo. of body-weight *per diem* is nearly the same in both (24—26 mg. for the dog, 26—30 mg. for man). Under ordinary conditions of diet, the methyl group of the lecithin and cephalin ingested can all be accounted for by the creatinine excreted. With excess of lecithin and cephalin this is not the case, although the creatinine excreted is increased. Creatine is present not only in striated muscle, but also in heart muscle and testis.

W. D. H.

Uniformity of Homogentisic Acid Excretion in Alcaptonuria. ARCHIBALD E. GARROD and T. SHIRLEY HELE (*J. Physiol.*, 1905, 33, 198—205).—The average excretion of homogentisic acid in all observed cases of alcaptonuria (except one—Zimper's) is fairly uniform. Its relationship to nitrogen excretion varies between very narrow limits, in spite of the fact that no simple standard diet has been adopted. It is more than probable that only one degree of alcaptonuria exists, namely, that the metabolic error is complete, and the homogentisic acid represents the whole of the tyrosine and phenylalanine of the proteids broken down.

W. D. H.

Relation between Scatole and the *p*-Dimethylaminobenzaldehyde Reaction of Urine. CHRISTIAN A. HERTER (*J. Biol. Chem. New York*, 1906, 1, 251—256).—In an intense form, the red colour given to urine by the addition of Ehrlich's reagent mentioned in the title is pathological. The administration of large quantities of blood to a dog does not affect this urinary reaction; the administration of 0.1 gram of indole has also negative results. Small quantities of scatole, however, given by the mouth markedly increase the reaction. Tryptophan has the same effect. It is probable that scatole or scatole derivatives originating in intestinal putrefaction may be the usual cause of the increased reaction in human urine.

W. D. H.

Acetonuria following Chloroform and Ether Anæsthesia. HELEN BALDWIN (*J. Biol. Chem. New York*, 1906, 1, 239—250).—The urine after anæsthesia has a high specific gravity, a strongly acid

reaction, and in 70 per cent. of the cases examined (40 in number) there was a marked acetone reaction, due to a disturbance of metabolism, probably in the liver cells. W. D. H.

Epidemic Diarrhœa. J. E. SANDILANDS (*J. Hygiene*, 1906, 6, 77—92).—Cows' milk may have a high bacterial content and yet not cause diarrhœa. Some preserved milks, although containing comparatively few bacteria, are a frequent cause of the ailment. The infection which leads to diarrhœa usually originates in the district in which the food is prepared, and is usually derived from the excrements of people suffering from diarrhœa. House flies are regarded as the most important carriers of the infection from the fæces to the food.

W. D. H.

Uric Acid Metabolism. MARCO ALMAGIA (*Beitr. chem. Physiol. Path.*, 1905, 7, 459—462). WILHELM PFEIFFER (*ibid.*, 463—465). MARCO ALMAGIA (*ibid.*, 466—472). **The Occurrence of Glyoxylic Acid in Urine.** RYOKICHI INADA (*ibid.*, 473—478).—The first paper of the series confirms the statements of Wiener and Schittenhelm that many of the mammalian tissues have the power of destroying uric acid and gives details as to the extent of this action. The second deals more fully with the kidneys, where the power is very great, but greater in man and herbivora than in the dog. The third shows that cartilage has the property of being able to absorb solutions of urates and then deposit them in crystalline form; this is of importance in view of gouty deposits. The last shows that glyoxylic acid, one of the decomposition products of uric acid, occurs in the urine. In herbivora fed on hay, the acid is also present, and is derived from the aromatic substances in the food.

W. D. H.

Excretion of Amino-acids in Gout and Leucæmia. A. LIPSTEIN (*Beitr. chem. Physiol. Path.*, 1905, 7, 527—530).—In gout and myelogenic leucæmia, the amount of amino-acids in the urine varies within normal limits.

W. D. H.

Solubility of Uric Acid in Blood Serum. ALONZO E. TAYLOR (*J. Biol. Chem. New York*, 1906, 1, 177—185).—From experiments with blood serum, the conclusion is drawn that the solvent power of blood for uric acid is about forty times that of water. This includes the amount held in solution by the water of the serum, that held by adsorption by the colloids, and that held in some complex combination. The second quantity is not inconsiderable, since a solution of neutral globulin in water will hold about five times the amount soluble in the same volume of water. But the largest quantity of the three is the last; in the complex combination referred to, the uric acid figures in all probability in the molecule. Some of the bearings of these observations on the pathology of gout are pointed out.

W. D. H.

Lipæmia and Diabetes. H. G. TWINEY and LEONARD S. DUDGEON (*J. Path. Bact.*, 1906, 11, 50—58).—A case of diabetes associated with lipæmia is described in full together with the autopsy. The lipæmia was first recognised during life by the ophthalmoscopic

examination of the retinal blood-vessels. There was, however, no interference with vision. Osmic acid staining of the fat granules was unsatisfactory possibly because their envelopes hinder its action. Good results were obtained by the use of Scharlach R. and Sudan III.
W. D. H.

Typhoid and Paratyphoid Bacteria and Sera. A. E. BOYCOTT (*J. Hygiene*, 1906, 6, 33—73).—*Bacillus paratyphosus* produces a typhoid-like illness. The diagnosis may usually be made from the agglutinative reactions of the serum. A fluid medium containing dulcitol is of great assistance in the isolation of the organism.
W. D. H.

Concentration of Antitoxin for Therapeutic Use. ROBERT B. GIBSON (*J. Biol. Chem. New York*, 1906, 1, 161—170).—The method is based on the fact that a saturated solution of sodium chloride will dissolve out from the mixed globulins (precipitated from serum by half-saturation with ammonium sulphate) the globulin which is antitoxic. The material so obtained is very potent, and is used in the New York hospitals with excellent results, including a comparative freedom from serum rashes.
W. D. H.

Action of Chloral Hydrate on the Heart. ERWIN ROHDE (*Chem. Centr.*, 1905, ii, 1544; from *Centr. Physiol.*, 19, 503—504).—The experiments were performed with the ventricle apex of the frog's heart treated with a 0.75 per cent. solution of chloral hydrate. The refractory period became shorter and disappeared; the "all or nothing" law no longer held, the amount of contraction being proportional to the strength of the stimulus, and rhythmic replies to continuous stimulation were no longer obtained. These appearances were also obtained with an atropinised heart, and inhibitory phenomena were thereby excluded. By the use of poisons, it is therefore possible to abolish the main characteristics of heart muscle, and make it behave like an ordinary muscle.
W. D. H.

Behaviour of Amino-acid administered to Animals. MAX PLAUT and HEINRICH REESE (*Beitr. chem. Physiol. Path.*, 1905, 7, 425—432).—After feeding dogs and men on alanine it is possible to obtain much more of that amino-acid from the urine than can be obtained by Embden and Reese's method (see this vol., ii, 108) under normal conditions.
W. D. H.

Behaviour of Toluidines in the Animal Organism. HERMANN HILDEBRANDT (*Beitr. chem. Physiol. Path.*, 1905, 7, 433—437. Compare Abstr., 1903, ii, 228).—When dimethyl-*p*-toluidine is given to animals, the same products are found in the urine as when *p*-dimethylaminobenzaldehyde is used (Jaffé, Abstr., 1905, ii, 186).

The introduction of methyl groups into the amino-radicle of *p*-aminobenzoic acid considerably lessens the poisonous nature of the acid, and so similarly with *p*-toluidine. The least active compound appears to be

the trimethyl compound (*p*-benzobetaine, $C_6H_4\langle\begin{smallmatrix} NMe_3 \\ CO \end{smallmatrix}\rangle O$, Abstr., 1904, i, 235). J. J. S.

Decomposition of Acids of the Propionic Series by Physiological Methods. RICCARDO LUZZATTO (*Beitr. chem. Physiol. Path.*, 1905, 7, 456—457).—When sodium hydracrylate (β -hydroxypropionate) is administered to dogs, no acids soluble in ether are formed. With sodium β -iodopropionate, the iodine is eliminated as iodide. Doses of 1 gram of sodium acrylate have toxic effects, and kynuric acid is found in the urine. J. J. S.

Action of Atropine and other Alkaloids on the Spontaneous Movements of Plain Muscle. G. BECK (*Chem. Centr.*, 1905, ii, 1545; from *Centr. Physiol.*, 19, 497—502).—The spontaneous movements observed in a ring of frog's stomach do not always disappear after treatment with atropine; after removal of the poison by Ringer's solution, spontaneous movements often appear. Strong solutions of atropine, however, act injuriously on the muscle. One per cent. solutions of cocaine abolish the movements. *apoc*deine and codeine act similarly. After treatment with a 1 per cent. solution of morphine, the movements may reappear after a long time.

W. D. H.

Behaviour of Strychnine in Birds. HANS MOLITORIS (*Zeit. angew. Chem.*, 1905, 18, 1977—1978).—Strychnine was administered to different kinds of birds either by the mouth or subcutaneously. By microchemical examination of the tissues, it is possible to recognise 0.00008 mg., Otto's colour reaction being used. The quantity absorbed necessary to cause death is extraordinarily small. Absorption is slow from the digestive canal. Hens, however, as was previously known, possess a high degree of immunity to the poison, not only on account of the slow rate of absorption, but because these animals possess the power of destroying what is absorbed.

W. D. H.

Reaction of Cells and Nerve-endings to certain Poisons. JOHN N. LANGLEY (*J. Physiol.*, 1905, 33, 374—414).—Nicotine causes prolonged contraction in certain muscles of the fowl, even after section of their nerves, or after paralysis is produced by curare. The nicotine contraction is lessened by a sufficient dose of curare; the two poisons are antagonistic, but nicotine is the more powerful. At the height of nicotine contraction, a galvanic current causes partial inhibition. Degeneration of the motor nerves leaves these effects unaltered, but there is increased responsiveness to nicotine, and the action of curare is less marked. As the axon endings are destroyed, the drugs must act on the muscle itself; but as the muscle responds to direct stimulation, the poisons cannot act directly on the contractile substance, but on other substances in the muscle which may be termed receptive substances. This deduction may be applied to other cells, and the majority of poisons ordinarily supposed to act on nerve-endings act on the receptive substances of the cells. As adrenaline acts on receptive

substances, it is probable that secretin, iodothyron, and other internal secretions also act on receptive substances, although the cells may not be connected with nerve fibres.

It may therefore be supposed that in all cells two constituents at least are present: (1) a chief substance concerned with cell function, and (2) receptive substances which may be acted on by chemical materials, or in certain cases by nervous stimuli. The receptive substance affects, or can affect, the metabolism of the chief substance. A cell may make motor or inhibiting receptive substances or both, and the effect of a nerve impulse depends on the proportion of the two kinds of receptive substance which is affected by the impulse. There are many other speculations arising out of the general idea propounded.

W. D. H.

Toxicity of Sea-water for Fresh-water Animals. C. W. WOLFGANG OSTWALD (*Univ. Calif. Publ. Physiology*, 1905, 2, 163—191. Compare Abstr., 1905, ii, 272).—Curves of the toxicity of sea-water of various concentrations up to 52 per cent. were constructed for the fresh-water *Gammarus*. The females are less resistant than the males. The effects were then investigated for the individual salts alone and in combinations with the others. Sodium chloride in the concentration in which it is contained in sea-water is much more toxic than sea-water. The toxicity of this salt is lowered more by potassium chloride than by any other salt. Calcium chloride acts similarly, but less strongly. Magnesium sulphate acts still more feebly, and has, further, a specific influence making the decline of the curves more gradual for all solutions which contain it. Magnesium chloride increases the toxicity in all combinations of salts. The toxic effects do not fit in with any physical or osmotic theory, but are specific chemical effects probably of the nature of coagulation. Certain unknown acids are also produced by the animals with increasing concentration of salts; these possibly are toxic also.

W. D. H.

Toxicity of Semen and Genital Products. GUSTAVE LOISEL (*Compt. rend.*, 1905, 141, 910—912).—The substances rejected by both ovaries and testis contain toxic materials; feeding invalids with eggs should therefore be undertaken cautiously. Extracts of sperm modify growth and exaggerate normal oscillations; injected into the veins, death may be the result. The symptoms vary with the species of animal, the sex, and the stage of incubation.

W. D. H.

Poisoning as the Result of eating the Seeds of Phaseolus Lunatus. A. ROBERTSON and A. J. WYNNE (*Zeit. anal. Chem.*, 1905, 44, 735—741).—Four persons out of seven who had made a meal of cooked *Phaseolus lunatus* (Kratok) beans died, the cause of death being hydrocyanic acid. In each case, hydrocyanic acid was present in the intestines and urine, but could not be detected in the stomach, the acidity of the latter hindering the decomposition of the glucoside. Experiments with the beans themselves showed that free hydrocyanic acid was only produced in the presence of alkali. The quantity of hydrocyanic acid obtained from various samples of the beans varied

from nothing in the white variety to 0·2 per cent. in certain dark-coloured beans examined. Although these beans may be used for food, it will be seen that their use is attended by great danger (compare Dunstan and Henry, *Abstr.*, 1904, ii, 71).

W. P. S.

Precipitins of Snake Antivenoms and Antisera. ANDREW HUNTER (*J. Physiol.*, 1905, 33, 239—250. Compare *Abstr.*, 1905, ii, 539).—Specific precipitins are produced by the injection of snake venom. These have no action on snake sera. Snake sera also lead to the appearance of specific precipitins which, however, also precipitate the corresponding venoms. There is no constant relation between the precipitating power and antitoxic value of an antivenom. Similarly, the amount of toxic substance in a venom bears no proportion to its content in precipitable substances. Consequently the precipitin-producing substances are not the toxins, or at any rate not the whole of the toxins; they are probably merely the coagulable proteids of the venom.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Behaviour of Aërobic Organisms towards Complete Withdrawal of Oxygen. WALTHER WILLIMSKY (*Arch. Hygiene*, 1905, 54, 375—385).—Aërobic organisms live with minimal traces of oxygen, and flourish better the more slowly the oxygen is withdrawn. If the oxygen is entirely removed, they, however, die, and the more suddenly the oxygen is removed the more rapid is the death. W. D. H.

Liquefaction of Gelatin by *Bacillus Cloacæ*. A. MACCONKEY (*J. Hygiene*, 1906, 6, 23—32).—*Bacillus cloacæ* liquefies gelatin very slowly, sometimes taking a month or more to do so. By appropriate methods, it is shown that the time may be shortened to a week, and so delay and inconvenience can be avoided. W. D. H.

Oxidation of Hydrogen and Methane by Micro-organisms. HERMANN KASERER (*Centr. Bakt. Par.*, 1905, ii, 15, 573—576; from *Zeit. Landw. Versuchswes. Oesterr.*, 1905, 8, 789).—Bacteria are present in soils which, in absence of light, assimilate carbon dioxide and at the same time, in presence of oxygen, oxidise hydrogen. Methane is utilised by soil organisms as a source of carbon. This explains why there is no accumulation of methane in the atmosphere (compare Söhngen, this vol., ii, 42). The presence of hydrogen and methane hinders the production of nitrites from ammonium salts. With abundant aëration, oxidation of hydrogen and nitrification may go on simultaneously, but with deficient aëration, nitrification only commences when the hydrogen is oxidised (compare van Iterson, *Centr. Bakt. Par.*, 1904, ii, 11, 692). N. H. J. M.

Utilisation of Atmospheric Nitrogen by Micro-organisms. R. THIELE (*Landw. Versuchs-Stat.*, 1905, **63**, 161—238).—Whilst there is no doubt that the *Azotobacter* has the power of fixing elementary nitrogen, it is questionable whether this property is specifically inherent, and it is possible that it may even be lost under normal conditions. In any case it must be assumed that fixation is less in soils where the optimum temperature is only occasionally reached. It will, however, be impossible to ascertain how the organism behaves under natural soil conditions until more exact methods are devised for determining very small variations in the amounts of nitrogen in soils.

N. H. J. M.

Intensive Nitrification. ACHILLE MÜNTZ and E. LAINÉ (*Compt. rend.*, 1905, **141**, 861—867).—The object of the experiments was to obtain a process for the production of nitrates sufficiently rapid for the needs of the country in time of war.

As a medium for nitrifying organisms, it was found that animal charcoal is far better than cinders, and that ten square decimeters gave, with a solution of 0.75 per cent. of ammonium sulphate, 8.1 grams of sodium nitrate per day. With stronger solutions, nitrification is less active. The difficulty is the evaporation of the large amounts of water, but this may be diminished by adding fresh ammonium salts to the nitrified solution until the nitrate begins to interfere with the process.

Experiments with soil to which 0.2 per cent. of ammonium sulphate was added produced nitrates at the rate of 350 grams per cubic metre per day, corresponding with 1750 kilos. of sodium nitrate per hectare in a bed 0.5 metre thick. Another soil, consisting of leaves, farmyard manure, and soil, yielded nearly twice as much nitrate. The limits to which nitrates may accumulate vary with different soils. Some light soils became sticky like clay; in others, nitrification continued until the chalk was exhausted. The highest amounts reached at present were 2.7 and 3.3 per cent. of sodium nitrate in the soil, whilst the water in the soil contained from 55 to 157 grams per litre.

N. H. J. M.

Probable Existence of Emulsin in Yeast. THOMAS A. HENRY and SAMUEL J. M. AULD (*Proc. Roy. Soc.*, 1905, **76 B**, 568—580).—When ordinary pressed yeast is added to an aqueous solution of amygdalin and the mixture kept for some time at 40°, the glucoside undergoes hydrolysis into hydrogen cyanide, benzaldehyde, and dextrose, the latter immediately undergoing alcoholic fermentation under the influence of zymase. In most of the experiments, the action ceases when about 70 per cent. of the amygdalin has been hydrolysed. Yeast juice (Buchner's zymase) and "zymin" bring about the same result; the latter is much less active than ordinary yeast. The hydrolytic action of yeast juice is not much affected by hydrogen cyanide and diminishes only very slowly on keeping, in both of which respects it differs from the behaviour of zymase. The action in question is not due to invertin, since it has been found, in agreement with Fischer (compare *Abstr.*, 1895, i, 6, 553), that the latter

enzyme only partially hydrolyses amygdalin to mandelonitrile-glucoside and dextrose.

The authors consider that the results obtained are due to the presence of emulsin in yeast, and adduce in support of their conclusion the facts that yeast induces the hydrolysis of salicin and arbutin, but not of sinalbin or digitalin; its activity is not affected by antiseptics, but is destroyed by small amounts of acids or alkalis; it is most active at 40°, and loses its activity on heating to 70°, in all of which respects, as well as in its action on amygdalin, it behaves exactly like emulsin.

G. S.

Influence of Temperature on the Rate of Development of Organisms. REGINALD O. HERZOG (*Zeit. Elektrochem.*, 1905, 11, 820—822).—The rule that a rise of temperature of 10° increases the velocity of a chemical reaction to two or three times its original value is shown to hold for the rate of formation of the ascospores of yeast, for the time required to double the number of yeast cells, for the time of germination of the seeds of several plants, and for the time of development of the eggs of fish. The rule only holds within comparatively narrow limits of temperature (compare Abegg, this vol., ii, 95).

T. E.

Influence of Electrodes on Germinating Seeds. H. MICHEELS and P. DE HEEN (*Bull. Acad. roy. Belg.*, 1905, 394—399).—Wheat grain was germinated in a series of vessels containing the same nutritive solution and subjected to the same electric current (from twelve Daniell elements), but with different electrodes.

The action of polarity is distinct from that resulting from the nature of the electrode. When aluminium and gold are employed together as electrodes, the greatest length of root is obtained on the aluminium side; when aluminium forms the cathode, the average weight of the neighbouring germinations is much greater than that of the germinations near the gold anode, whilst when the electrodes are reversed the weights produced are about the same. As regards aluminium, therefore, the nature of the electrode is of more influence than its polarity. Further experiments in which the effect of the latter was eliminated showed that it is towards the cathode that the development of roots is most marked.

N. H. J. M.

Comparison of the Actions of Aluminium, Zinc, and Carbon Electrodes on Germination. H. MICHEELS and P. DE HEEN (*Bull. Acad. roy. Belg.*, 1905, 400—402).—The greatest effect was produced with aluminium electrodes, but zinc, although less favourable than aluminium, has a distinct action on germination.

N. H. J. M.

Action of Colloidal Solutions of Tin on Germinating Seeds. H. MICHEELS and P. DE HEEN (*Bull. Acad. roy. Belg.*, 1905, 310—318).—Colloidal solutions of tin stimulate the germination of wheat and oats, &c., and considerably increase the growth of roots. Similar solutions which have been twice filtered and contain only 0.0075 gram of solid matter per litre have much the same effect.

The action is diminished by an electric current or by addition of some substance which causes flocculation.

The stimulating effect is attributed to the uniform liberation of energy in all directions by the suspended particles resulting from the absence of ionic equilibrium. According to the nature of the suspended substance, its influence will be favourable or unfavourable to the organism.

N. H. J. M.

Development of Amylase during Germination. JEAN EFFRONT (*Compt. rend.*, 1905, 141, 626—628).—The saccharifying power of seeds increases irregularly as germination proceeds until a maximum is reached, after which it diminishes. The liquefying power increases more slowly but more regularly, and after the maximum is reached remains the same for some time.

Malt which has been prepared in darkness and then exposed to sunlight retains its liquefying power a long time, but loses its saccharifying power.

Phosphates and 0.05 per cent. copper sulphate are favourable to germination. Ammonium chloride increases the liquefying power and xylene (1 c.c. per litre) increases both the liquefying and saccharifying power. Bleaching powder in presence of alkali is favourable to germination, but hinders the formation of diastase; in absence of alkali, it increases both the power of germination and the amylase.

N. H. J. M.

Development of Green Plants grown without Carbon Dioxide in Artificial Soil containing Amides. JULES LEFÈVRE (*Compt. rend.*, 1905, 141, 664—665, 1035—1036).—Three pots (*A*, *B*, and *C*), containing sand and mineral food, two of them (*A* and *C*) with an amide as well, were exposed to the air for some weeks and watered with ordinary water. Basil was sown in two pots (*A* and *B*), and when the plants were 4 cm. high the three pots were placed under bell-jars with baryta.

There was a slight liberation of carbon dioxide from pots *A* and *B* which was without effect on the plants in *B*. In pot *A*, which contained an amide, the plants developed rapidly.

The results also show that the carbon dioxide of the soil is not absorbed by the roots, or, if so absorbed, is not utilised.

The second paper describes experiments with *Lepidium sativum*. In absence of light and carbon dioxide, the plants failed completely in artificial soil containing amides. In presence of light, the plants, under otherwise similar conditions, doubled their weight in seven days.

N. H. J. M.

Increase in the Dry Weight of Green Plants grown in Light, without Carbon Dioxide in Artificial Soil containing Amides. JULES LEFÈVRE (*Compt. rend.*, 1905, 141, 834—836).—Experiments with cress and basil showed that the dry matter of the plants rapidly increased in presence of an amide, but without carbon dioxide. The growth is normal and not a mere watery shoot (compare preceding abstract).

N. H. J. M.

Structure of Plants developed in Presence of Light, without Carbon Dioxide and with Organic Substances. MOLLIARD (*Compt. rend.*, 1906, 142, 49—52).—Plants grown in a confined space without carbon dioxide, but with organic nutrient, acquire a structure similar to that of underground organs. Sometimes tissues are formed with multinucleate cells, as in the case of certain galls. N. H. J. M.

Influence of Light of Various Kinds on the Migration of the Proteids in Wheat Grain. J. DUMONT (*Compt. rend.*, 1905, 141, 686—688).—The wheat was enclosed in boxes with sides and top of coloured glass. Accumulation of nitrogen in the grain was greatest under the influence of brown ("bistre foncé") light, then green, blue, and red. The most favourable kind of light is, therefore, that which interferes least with the functions of the chlorophyll.

N. H. J. M.

Insoluble Alkaline Compounds in Living Vegetable Tissues. MARCELLIN BERTHELOT (*Compt. rend.*, 1905, 141, 793—802).—The insoluble organic matter of *Festuca* contains small amounts of potassium as well as calcium, aluminium, phosphoric acid, and silica, &c. When digested with solutions of potassium acetate, the insoluble organic matter fixes a certain amount of potassium, and at the same time liberates calcium; with solutions of calcium acetate, there is fixation of calcium and liberation of potassium. Chlorides of potassium and calcium have scarcely any effect. Wood charcoal contains potassium compounds insoluble even in dilute hydrochloric acid. It has the power of fixing potassium or calcium when digested with potassium or calcium acetate.

The results indicate that some analogy exists between the insoluble and polymerised acids of fresh plants, of humic substances, and of their mineral products.

N. H. J. M.

Insoluble Potassium Compounds in Humic Matters. MARCELLIN BERTHELOT (*Compt. rend.*, 1905, 141, 1182—1187).—Wood charcoal (60 grams) treated with 1 per cent. hydrochloric acid (600 c.c.) at 100° and washed with 10—12 litres of water retained 5—6 per cent. of its total potassium and 5 per cent. of its calcium, which are present as organic compounds, the amounts of silica, iron, and alumina present being too small to account for their retention. When the charcoal, treated as described, was digested with dilute solutions of potassium acetate, the amounts of potassium and calcium remained the same; whilst with calcium acetate the calcium remained the same and the potassium slightly diminished.

N. H. J. M.

Distribution of Manganese in the Different Parts of *Lupinus Albus*. NAPOLEONE PASSERINI (*Bol. Ist. Agrar. Scandicci*, 1905, [ii], 6, 3—14).—The soil in which the plants were grown contained, when dried at 100°, 0.068 per cent. of manganese. The different parts of the plants, dried at 100°, contained the following amounts of crude

ash. The results relating to manganese are given as percentages in the ash.

	Leaves.	Legumes.		Stems.	Branches.	Seeds.	Roots.	Nodules.
		(1.)	(2.)					
Ash	8.267	3.726	3.280	2.286	2.021	2.102	3.910	10.400
Mn ₂ O ₃ ...	12.436	7.080	5.927	4.580	4.231	2.190	1.536	0.377

The legumes from the middle (1) of the plant were separated from those at the ends (2), and the upper portions of the stems were included with the branches.

Pot experiments are described in which lupins were grown in sand containing 0.0002 per cent. of manganese, both without further addition of manganese and with addition of manganese carbonate. The yield of fresh produce was about the same in both cases. The dry matter of the plants without manganese carbonate contained 0.0095 per cent. of Mn, those with manganese 0.0636 per cent. N. H. J. M.

Juglone [**Hydroxynaphthaquinone**]. BRISSEMORET and R. COMBES (*Compt. rend.*, 1905, 141, 838—840).—Most plants of the order *Juglandaceæ* contain hydroxynaphthaquinone, to which the physiological properties of walnuts are in part due (compare Bernthsen and Semper, *Abstr.*, 1885, 546, and Mylius, *ibid.*, 803).

N. H. J. M.

Formation and Quantitative Variations of the Cyanogenetic Principle of Sambucus Nigra. L. GUIGNARD (*Compt. rend.*, 1905, 141, 1193—1201. Compare *Abstr.*, 1905, ii, 604).—The amount of cyanogenetic glucoside in the leaves of *Sambucus nigra* diminishes only slightly with the age. At the end of the vegetative period, the glucoside does not migrate to the stems, but remains in the leaves until they fall off. N. H. J. M.

Brown Pigment of Phæophyceæ and Diatoms. HANS MOLISCH (*Chem. Centr.*, 1905, ii, 1607; from *Bot. Zeit.*, 1905, i, 132—144).—The assumption that the brown colour of living chromatophores depends in the case of the brown algæ (phæophyceæ) on the presence of the brown pigment, phycophæin, which masks the green colour of the chlorophyll, is incorrect. The phycophæin, which may be isolated by boiling the algæ, is not contained in the living cell, but is only formed from a chromogen after the death of the organism. A "brown chlorophyll" or phæophyll is contained in the living chromatophore, and the rapid change to green which takes place when the algæ are exposed to hot air or placed in hot water, alcohol, or other liquids is caused by the conversion of this substance into ordinary chlorophyll. The diatoms behave in a similar manner and the living chromoplasts of the orchid *Neottia nidus avis* also contain a brown pigment which is rapidly converted into chlorophyll on the death of the plant. The solution of crude chlorophyll prepared by extracting the phæophyceæ or diatoms with absolute alcohol not only contains chlorophyll and carotin, but a new compound, *leucocyanin*, which, when treated with very dilute hydrochloric acid, yields a bluish-green pigment, phæocyanin. E. W. W.

Emulsin; General Existence of the Ferment in Orchids. LÉON GUIGNARD (*Compt. rend.*, 1905, 141, 637—644).—Emulsin was found in the roots of every variety of orchid examined, both indigenous and exotic; it was not always detected in the tubers, stems, and leaves, and, when present, was in much smaller quantity than in the roots. The amounts of hydrogen cyanide produced by 30 grams of substance and 0.2 gram of amygdalin in the case of (1) *Goodyera repens* and (2) *Epipactis latifolia* were as follows: Roots, (1) 0.0064, (2) 0.0045; stems, (1) 0.0021, (2) 0.0010; and leaves, (1) 0.0011, (2) 0.0031.

In the case of exotic orchids, the roots (30 grams) of eight varieties yielded amounts of hydrogen cyanide varying from 0.001 gram (*Stanhopea tigrina*) to 0.009 gram (*Cypripedium hirsutissimum*).

N. H. J. M.

Composition of the Dried Grapes used in the Preparation of Tokay Wine. LUDWIG KRÄMSKY (*Zeit. Nahr. Genussm.*, 1905, 10, 671—686).—The following results were obtained by the analysis of samples of the dried grapes from vines grown on the Hegyalya hills, and employed in the preparation of Tokay: water, 39.42; total sugar (as invert sugar), 30.28; dextrose, 19.47; lævulose, 7.42; total acid (as tartaric), 1.66; total tartaric acid, 1.46; free tartaric acid, none; potassium hydrogen tartrate, 1.83; malic acid, 0.78; tannin, 0.02; total nitrogen (organic), 0.13; ash, 1.12; phosphoric oxide, 0.10 per cent.

These dried grapes differ from raisins and similar fruits in several particulars. They contain about 2.5 times as much dextrose as lævulose, whilst in raisins the greater half of the total sugars is lævulose. Raisins contain only traces of malic acid, and to the presence of an appreciable amount of this acid in the Tokay grapes is attributed the characteristic bouquet of Tokay wine. The Tokay grapes are not dried so much as are raisins, sultanas, &c.

W. P. S.

Bacteriological and Chemical Studies of Soils from the Experimental Fields. FERDINAND WOHLTMANN, H. FISCHER, and PH. SCHNEIDER (*Bied. Centr.*, 1905, 34, 805—807; from *J. Landw.*, 1904, 52, 97).—The power of decomposing nitrogenous substances is increased in soils by manuring with lime and still more by complete mineral manure, whilst ammonium sulphate has the opposite effect. Under natural conditions, the decomposition will vary according to temperature, &c., and in practice is not merely a question of decomposing nitrogen compounds, the nature of the decomposition being of importance.

Nitrification is favoured by lime and magnesia; it was least active on the plots receiving phosphoric acid, potassium, and ammonium sulphate. Denitrification is also assisted by lime.

N. H. J. M.

Effect of Plant Growth and of Manures on the Retention of Bases by the Soil. ALFRED D. HALL and NORMAN H. J. MILLER (*Proc. Roy. Soc.*, 1905, B, 77, 1—32).—The Rothamsted soils generally contain about 3 per cent. of calcium carbonate, nearly all of which is

due to former applications of chalk. Determinations made in numerous samples from different plots of Broadbalk, Agdell, and Hoos Fields, taken at different dates from 1856 to the present time, show that the soils of the unmanured plots lose in drainage on the average about 1000 lbs. of calcium carbonate per acre per annum. This agrees closely with results derived from analyses of field drainage by Creydt, von Seelhorst, and Wilms (Abstr., 1902, ii, 45; compare Voelcker, this Journal, 1871, 24, 276; and Miller, *Proc.*, 1902, 18, 89).

The loss of calcium carbonate is increased when ammonium salts are employed by an amount equivalent to the acid of the manure. Sodium nitrate and farmyard manure diminish the loss.

Analyses of wheat plants grown in water-culture and of the solutions themselves showed that the plants take up an excess of acid from the salts supplied, leaving behind a corresponding excess of base. This explains how it is that, despite losses by nitrification, soils which contain only minute amounts of calcium carbonate (examples of such soils are given) are able to maintain a neutral condition (compare Lawes and Gilbert, *Jour. Roy. Agric. Soc. Eng.*, 1894, 55, 640; Warrington, Abstr., 1900, ii, 570). The experiments also furnished evidence that the roots of the plants did not excrete any organic acid or other organic matter (compare Czapek, *Jahrb. Wiss. Bot.*, 29, 321; Kossowitsch, Abstr., 1903, ii, 234).

Finally it is shown that calcium oxalate and other organic salts are converted into carbonate by soil organisms (Smøger, Abstr., 1879, 737).
N. H. J. M.

Behaviour of "Soluble" Phosphoric Acid and its Movements in the Soil. WILHELM HOFFMEISTER (*Bied. Centr.*, 1905, 34, 817—820. Compare Abstr., 1898, ii, 538).—The diminution in the soluble phosphoric acid of soils seems to be only due to assimilation by plants and not to conversion into insoluble forms.

Notwithstanding the withdrawal of phosphoric acid from the sub-soil, the relative amount of soluble phosphoric acid increases downwards, indicating a downward movement of phosphoric acid in the soil.

Different varieties of peat which in their natural condition did not contain determinable amounts of phosphoric acid soluble in ammonium humate yielded 0.006 to 0.061 per cent. when heated at 160°.

N. H. J. M.

Manurial Questions. PAUL WAGNER (*Bied. Centr.*, 1905, 34, 809—813; from *Düngungsfragen*, 1904, Heft. 6. Compare Abstr., 1904, ii, 768).—Experiments with barley, oats, rye, and potatoes showed that the average gain with sodium nitrate was twice that produced by ammonium salts. This is attributed to loss of ammonia as carbonate. The most suitable soils for ammonium salts are loams containing moderate amounts of calcium carbonate, and it may perhaps be desirable to plough the manure in.

Vines should be manured with sodium nitrate in addition to farmyard manure. Potassium and phosphoric acid are only effective when plenty of nitrogen is at the disposal of the vines.
N. H. J. M.

Nitrates and Nitrites as Manures. THÉOPHILE SCHLÆSING, jun. (*Compt. rend.*, 1905, **141**, 745—746).—Pot experiments with maize grown in soil showed that calcium and sodium nitrites produced the same results as sodium nitrate, and calcium nitrate prepared by Birkeland and Eyde's process. N. H. J. M.

Factors which affect the Manurial Value of the Phosphoric Acid of Bone Meal. HENRIK G. SÖDERBAUM (*Landw. Versuchs-Stat.*, 1905, **63**, 247—262. Compare *Abstr.*, 1904, ii, 79).—Ammonium salts and organic nitrogen compounds are more favourable than sodium nitrate as regards the utilisation of bone meal. In some years, according to the season, the total yield was doubled, and the yield of grain (which is more influenced than the straw) trebled.

Ammonium salts, as compared with sodium nitrate, have a similar effect when employed in conjunction with Algeria phosphate and with precipitated tricalcium phosphate, but not with superphosphate, basic slag, and precipitated dicalcium phosphate.

When no considerable amounts of calcium were present, bone meal (with ammonium salts) was equal to superphosphate.

N. H. J. M.

Favourable Employment of Manganese as Manure. GABRIEL BERTRAND (*Compt. rend.*, 1905, **141**, 1255—1257).—The soil on which the experiments were made was clayey and contained 0.057 per cent. of manganese soluble in hydrochloric acid and 0.024 per cent. soluble in boiling acetic acid. Oats were grown on two plots of 20 ares, both of which had the usual manures and one pure manganese sulphate at the rate of 50 kilos. per hectare.

The application of manganese sulphate resulted in a gain of 17.4 per cent. of grain and of 26.0 per cent. of straw. The grain produced under the influence of manganese weighed 46.5 kilos. per hectolitre as compared with 44 kilos. without manganese. The grain from both plots contained the same amount of manganese (0.000004 per cent.) (compare Passerini, this vol., ii, 117).

N. H. J. M.

Analytical Chemistry.

Methods of Refractometry. F. LÖWE (*Zeit. Elektrochem.*, 1905, 11, 829—831).—The applications of the refractometer in quantitative analysis and the advantages of different types of instrument are discussed.
T. E.

Gas Analysis Apparatus. JOHN S. HALDANE (*J. Hygiene*, 1906, 6, 74—76).—A simplification of the author's earlier form of apparatus is described and figured.
W. D. H.

Estimation of Acids in Waste Gases. F. HENZ (*Zeit. angew. Chem.*, 1905, 18, 2002).—The apparatus, which somewhat resembles a German tobacco-pipe, is half filled with glass beads, and 25 c.c. of normal alkali are introduced. By means of a large earthenware aspirator, 100 litres of the gas are drawn through the apparatus. The solution is now transferred to a beaker and titrated with seminormal acid, the liquid is put back into the pipe, re-emptied into the beaker, and again titrated; this operation may be repeated a third time. The difference between the titration and the check represents the acidity of the gas.
L. DE K.

Estimation of Hydrogen Peroxide in Milk and the Preservation of Milk by this Substance. SAMUEL AMBERG (*J. Biol. Chem. New York*, 1906, 1, 219—228).—Hydrogen peroxide is described as an “apparently harmless” preservative for milk. It inhibits the growth of many bacteria without destroying them. The colorimetric method with titanium peroxide for its estimation is recommended.
W. D. H.

Analysis of Electrolytic Chlorine. FREDERICK P. TREADWELL and W. A. K. CHRISTIE (*Zeit. angew. Chem.*, 1905, 18, 1930—1934).—The joint amount of chlorine and carbon dioxide is found by absorption with a 5 per cent. solution of sodium hydroxide, and the hypochlorite formed is estimated by titrating with *N*/10 arsenious acid (Treadwell's process). Owing, however, to a slight formation of chlorate, the results are about 0.7 per cent. too low. The authors have therefore modified this method, and absorb the chlorine in a standardised solution of potassium dihydrogen arsenite, thus avoiding formation of chlorate. The carbon dioxide is then absorbed by aqueous potassium hydroxide. The excess of arsenious acid is titrated by means of standard iodine. For minute details and illustrations of the apparatus, the original paper should be consulted. L. DE K.

Estimation of Iodine in Aristols [Iodised Thymols]. H. CORMIMBŒUF (*Ann. Chim. anal.*, 1905, 10, 453—454).—0.5 gram of the sample is intimately mixed with 3 grams of dry sodium carbonate and heated in a nickel crucible until the organic matter has burnt off; the heat is then raised until the mass begins to melt. When cold, the residue is dissolved in water, and to the filtrate is added half its bulk of ammonia. The iodine is now precipitated by cautious addition of silver nitrate and weighed as silver iodide. The filtrate may still contain chlorine, as this often occurs in considerable quantity in commercial aristols; this may be precipitated by acidifying the filtrate with nitric acid and adding more silver nitrate. The silver chloride is then collected and weighed.
L. DE K.

Estimation of Oxygen in Copper. LEONARD ARCHBUTT (*Analyst*, 1905, 30, 385—390).—Results of many estimations are given showing that the oxygen present in copper is completely removed by heating the sample in a current of hydrogen (Abstr., 1900, ii, 756), and that the thickness of the pieces of copper taken for the estimation has

little, if any, influence on the results obtained if the heating is prolonged sufficiently. Fine turnings and sawings yield the same amount of oxygen as 0.25 inch cubes of the same sample. In some of the experiments, the copper was heated to a red heat, and in others to as high a temperature as could be obtained, but the author does not consider that the actual temperature makes much difference. A number of microphotographs of deoxidised copper are also given.

W. P. S.

Estimation of Ozone. FREDERICK P. TREADWELL and E. ANNELER (*Zeit. anorg. Chem.*, 1905, 48, 86—97. Compare Ladenburg and Quasig, *Abstr.*, 1901, ii, 420; Ladenburg, *Abstr.*, 1903, ii, 237).—The authors confirm the accuracy of Ladenburg's method of estimating ozone (*loc. cit.*—absorption in neutral potassium iodide solution, acidification, and titration of iodine set free with sodium thiosulphate), but find that still better results are obtained if the ozone, instead of being bubbled through the iodide solution, is collected in a glass bulb, into which the iodide solution is subsequently introduced. The excess of iodine set free when acid solution of potassium iodide is used is due to the formation of hydrogen peroxide, since the latter substance can be detected by the titanous acid test.

Potassium bromide cannot be used instead of the iodide, as the results both in acid and neutral solution are too low; the arsenious acid method is inconvenient, and does not give accurate results when the proportion of ozone is small. The sodium hydrogen sulphite method (Ladenburg, *loc. cit.*) is also inconvenient, and gives rather too high results.

G. S.

Estimation of Sulphur in Petroleum and Bituminous Minerals. FREDERIC C. GARRETT and E. L. LOMAX (*J. Soc. Chem. Ind.*, 1905, 24, 1212—1213).—From 0.7 to 1.5 gram of the substance is placed in a small platinum crucible, intimately mixed with 3 or 4 grams of a mixture of four parts of calcium oxide with one part of sodium carbonate, and the crucible then completely filled with latter mixture. A larger platinum crucible is now placed over the smaller one (mouth downwards), the whole inverted, and the space between the two crucibles filled with the lime-sodium carbonate mixture. After closing the mouth of the crucible with a thick piece of asbestos board, the apparatus is placed in a muffle furnace heated to bright redness. Distillation commences in about two minutes, and as soon as a flame appears the asbestos may be removed. The heating is continued for two hours, at the end of which time the mixture is brought into water, the sulphides, &c., are oxidised by the addition of bromine, and the solution then acidified, filtered, and precipitated with barium chloride as usual. Experimental proof is given that the method is trustworthy.

W. P. S.

Estimations of Sulphate and Sulphur. OTTO FOLIN (*J. Biol. Chem. New York*, 1906, 1, 131—160).—A discussion of the method of estimating sulphates as barium sulphate in view of the recent discovery of chlorine in barium sulphate precipitates (Hulett and Duschak,

Abstr., 1904, ii, 616) leads to suggesting means of overcoming this and other difficulties, with special reference to the determination of sulphates in the urine. Previous work appears to be untrustworthy. A method for estimating total sulphur in urine by means of sodium peroxide is also given with full details. W. D. H.

Estimation of Sulphurous Acid in Foods and Sulphur in Coal-gas. TH. SCHUMACHER and E. FEDER (*Zeit. Nahr. Genussm.*, 1905, 10, 649—659).—Whilst the method previously described by the authors (Abstr., 1905, ii, 856) gives sufficiently accurate results in the case of pure sulphite solutions, such is not the case when organic matter is present, and the method is consequently not applicable to the estimation of sulphurous acid in meats, dried fruits, &c. A modification of the process is now described which gives trustworthy results. It consists in distilling the article of food, after acidifying with phosphoric acid, in a current of carbon dioxide and collecting the distillate in a receiver containing a known volume of standardised potassium iodate solution. The iodine liberated by the sulphurous acid is expelled from the receiver by boiling the contents of the latter and the remaining iodate is titrated with *N*/10 thiosulphate solution after the addition of potassium iodide and sulphuric acid. For the estimation of sulphur in coal-gas, 2 cubic feet or more of the gas are burnt and the products of combustion drawn by means of a current of air through a known volume of iodate solution. The iodate remaining unreduced is then titrated. W. P. S.

Estimation of Sulphuric Acid by means of Barium Chloride in the Presence of Interfering Substances. GEORG LUNGE and R. STIERLIN (*Zeit. angew. Chem.*, 1905, 18, 1921—1930).—The conclusions arrived at by the authors are as follows. When estimating sulphur in pyrites by Lunge's ammonia method, the presence of copper causes no error. Small quantities of zinc are also harmless, but if large quantities of this metal are present, unsatisfactory results are obtained. It is recommended that the barium chloride solution should be added all at once; slight errors due to solubility of barium or to incomplete precipitation are then fully compensated by occlusion of barium chloride. L. DE K.

Estimation of Tellurous and Telluric Acids. ARMAND BERG (*Bull. Soc. chim.*, 1905, [iii], 33, 1310—1312).—The method is based on the production of tellurium chloride by the action of hydrogen chloride on tellurous and telluric acids or their salts. A weighed quantity of the substance is placed in a hard glass combustion tube into which at one end a current of dry hydrogen chloride can be passed. The other end of the tube is drawn out, bent at right angles, and connected to the first of two U-tubes each containing 5 c.c. of water. The porcelain boat is heated, a steady current of hydrogen chloride being maintained meanwhile. The chloride formed is driven forward and collected for the most part in the narrow drawn-out end of the combustion tube, whence, when the operation is finished, it is washed out by "sucking back" in succession the quantities of water contained in

the two U-tubes. The solution is placed in a tared porcelain crucible and, after the addition of some nitric acid, evaporated to dryness on a sand-bath, and the residue heated so as to produce tellurous anhydride, which is weighed. In the case of tellurites and tellurates, the chlorides left in the porcelain boat may be weighed. The method cannot be used with compounds containing mercury, chromium, or other substances which yield volatile chlorides. T. A. H.

Estimation of Nitrous and Nitric Acids. JAKOB MEISENHEIMER and FRIEDRICH HEIM (*Ber.*, 1905, **38**, 4136).—A reply to Raschig (this vol., ii, 50). The method previously described (*ibid.*, 49) is for the estimation of the two acids in presence of one another. J. J. S.

Analysis of Chili Saltpetre. R. BENSEMANN (*Zeit. angew. Chem.*, 1905, **18**, 1972—1974).—A recapitulation of the oxalic acid process (*Abstr.*, 1905, ii, 481, 555) illustrated with practical examples. L. DE K.

Estimation of Nitric Acid in Soils. BUHLERT and FICKENDEY (*Landw. Versuchs-Stat.*, 1905, **63**, 239—246).—The fresh soil (2 kilos.) is shaken for a quarter of a minute at intervals of five minutes during half an hour with 2—3 litres of water. It is then allowed to settle and filtered. A portion of the filtrate (400—500 c.c.) is evaporated down with a few drops of sodium hydroxide and analysed by Schloesing's method. In the case of soils which will not filter, 2 per cent. of sodium chloride is added and the desired amount of extract obtained with a pipette.

Prolonged extraction is to be avoided, as it may result in very considerable losses of nitrate. N. H. J. M.

Action of Acetylene on Iodine Pentoxide. GEORGE F. JAUBERT (*Compt. rend.*, 1905, **141**, 1233—1234).—The author states that Lévy and Pécoul's method for estimating carbon monoxide in air (*Abstr.*, 1905, ii, 203) would give false indications in the case of air containing acetylene, as this reduces iodine pentoxide according to the equation $I_2O_5 + C_2H_2 = I_2 + 2CO_2 + H_2O$. M. A. W.

Estimation of Carbon Monoxide in Air by means of Iodine Pentoxide. ARMAND GAUTIER (*Compt. rend.*, 1906, **142**, 15).—A reply to Jaubert (preceding abstract). The author has already described the reducing action of acetylene on iodine pentoxide and the correction to be applied in estimating carbon monoxide by means of iodine pentoxide in air containing acetylene (compare *Abstr.*, 1901, ii, 232). M. A. W.

Estimation of Silicon in Presence of Silica. M. PHILIPS (*Zeit. angew. Chem.*, 1905, **18**, 1969—1972).—The usual separation by treating the ignited mixture with hydrofluoric acid is untrustworthy, as silicon is somewhat oxidised on ignition, and is, moreover, strongly attacked by hydrofluoric acid. Good results may, however, be obtained by heating the mixed silica and silicon with a 30 per cent.

solution of potassium hydroxide and collecting the hydrogen evolved in a gas burette. Two mols. of hydrogen are liberated for each atom of silicon.

L. DE K.

Determination of Rare Gases in Natural Gaseous Mixtures. CHARLES MOUREU (*Compt. rend.*, 1906, 142, 44—46).—The paper contains a diagram of the apparatus and a description of the method employed by the author for estimating and examining rare gases from natural sources. The gas (about 300 c.c.) is first circulated through a series of tubes containing soda lime, phosphoric oxide, heated lime and magnesium, and heated copper oxide, to remove carbon dioxide, moisture, oxygen and nitrogen, or hydrogen and combustible material respectively. The purity of the gas is then tested by passing a sample through a second series of tubes, which are practically the first series in miniature, into a Plucker tube in which the spectrum is examined. Just before entering the last tube, the gas passes through a tube containing selenium to remove mercurial vapour. When the spectrum of the gas contains only lines and bands of rare gases, the Plucker tube is sealed off and the volume of the residual gas measured over mercury.

M. A. W.

General Method for the Separation of Metals without using Hydrogen Sulphide. ERICH EBLER (*Zeit. anorg. Chem.*, 1905, 48, 61—85).—With the object of avoiding the inconveniences attending the use of hydrogen sulphide in qualitative analysis, the author has devised a method of separation for all the common metals, based on the very different behaviour of metallic hydroxides towards ammonia. Whereas some are quite insoluble in it, others form stable complex compounds, soluble in excess of the reagent.

Tin, antimony, and arsenic compounds, as well as phosphoric acid, halogens, and complex cyanides, interfere with the working of the method and have to be removed; convenient methods of effecting this are described. The chief group reagents, with the metals belonging to each group, are as follows:

Group reagent.	Metals precipitated.
Hydrochloric acid	Ag.
$\text{NH}_4\cdot\text{OH}$, HCl and $\text{NH}_4\cdot\text{OH}$	Fe, Pb, Bi, Al, Cr, Hg.
HCl dilute and $\text{NH}_4\cdot\text{CNS}$	Cu.
$\text{NH}_4\cdot\text{OH}$ and $\text{NH}_4\cdot\text{SH}$	Mn, Zn, Cd, Ni, Co.

The salts of the alkalis and alkaline earths, which remain in solution, can be separated by the ordinary methods. Hydroxylamine hydrochloride is used in the second group to secure complete precipitation of iron and to prevent partial precipitation of manganese by oxidation.

For full details, the original paper must be consulted. G. S.

Separation of Barium from Strontium and Calcium by Precipitation as Chromate. ANTON SKRABAL and L. NEUSTADTL (*Zeit. anal. Chem.*, 1905, 44, 742—755).—The following procedure

is recommended for the separation of barium from calcium and strontium by the chromate method. An excess of neutral ammonium acetate is added to the neutral or feebly acid solution of the mixed salts. The mixture is then boiled and stirred while a 10 per cent. ammonium dichromate solution is added drop by drop. When cold, the clear supernatant liquid is decanted on to a filter and the precipitate washed by decantation with dilute ammonium acetate solution until a colourless filtrate is obtained. The small quantity of precipitate on the filter is now dissolved in a little warm dilute nitric acid and the solution added to the beaker containing the bulk of the precipitate. Sufficient nitric acid is added to dissolve the latter, the solution is rendered neutral by the addition of ammonia, boiled, and ammonium acetate solution added drop by drop. The mixture is then cooled slowly and the precipitate collected on a filter and washed with cold dilute ammonium acetate solution. After drying, the precipitate is detached as far as possible from the filter and ignited carefully in a platinum crucible, the filter being ignited separately and the ash added to the crucible. The strontium and calcium present may be estimated in the filtrate in the usual manner.

W. P. S.

Estimation of Cadmium by means of the Rotating Cathode. CHARLES P. FLORA (*Amer. J. Sci.*, 1905, [iv], 20, 454—455. Compare Abstr., 1905, ii, 855; this vol., ii, 52).—Cadmium nitrate is ill-fitted for electrolytic estimation except in presence of potassium cyanide; from a solution containing 1 per cent. or more of free nitric acid the cadmium is not deposited by the current. A summary of the previous experiments is given.

L. DE K.

Estimation of Cadmium as Oxide. CHARLES P. FLORA (*Amer. J. Sci.*, 1905, [iv], 20, 456—458).—The estimation of cadmium as oxide, obtained by ignition of the carbonate, gives unsatisfactory results when the precipitate is collected on an ordinary filter. The author, however, states that by using an asbestos filter placed in a Gooch crucible, and then heating to constant weight at a red heat, very accurate and concordant results may be obtained. The use of potassium hydroxide as a precipitant for cadmium cannot be recommended.

L. DE K.

Analysis of Aluminium and its Chief Alloys. CARLO FORMENTI (*Chem. Centr.*, 1905, ii, 1739—1740; from *Boll. Chim. Farm.*, 44, 661—675).—The original paper contains a description of the method of sampling commercial aluminium, the determination of its sp. gr., and the estimation of aluminium, silicon, iron, copper, sodium, carbon, lead, nitrogen, sulphur, phosphorus, arsenic, &c. The analyses and sp. gr. of ten samples are quoted in the abstract; the sp. gr. varied from 2.69 to 2.73, whilst the percentage of aluminium was from 98.33 to 99.581, of silicon from 0.103 to 1.17, and of iron from 0.22 to 0.624. The distribution of the silicon is of importance in reference to the use of the metal for culinary purposes, since its accumulation at different points considerably decreases the durability of the vessel.

Gold bronze from the Neuhausen factory was found to contain 3—5 per cent. of aluminium; steel bronze 8.5 of aluminium and 1 of silicon, "P.B." bronze 8.5 of aluminium and 2 of silicon; acid bronze "C" 10 of aluminium, and diamond bronze "D" 10 of aluminium and 2 of silicon. "*Laschenmetall*" is prepared from 88—92.5 parts of aluminium bronze containing 5 per cent. of aluminium, 7.5—10 of tin, and 62 parts of zinc, whilst Hercules metal No. 2 consists of 50 parts of aluminium bronze containing 2.5 per cent. of aluminium and 30 of zinc. For analysis, 3—4 grams of turnings are dissolved in dilute nitric acid and the silicon determined in the residue after evaporating the solution, acidifying with sulphuric acid, and diluting with water. The copper is estimated by an electrolytic method and the aluminium by precipitation with ammonia or by difference.

Aluminium brass is ordinary brass to which aluminium has been added. It is analysed by treating with dilute nitric acid and estimating the tin in the insoluble residue. The copper is determined electrolytically and the zinc by precipitation with ammonium sulphide, whilst the iron and alumina are estimated in the filtrate in the usual way. "Aluman" is an aluminium brass. "Argentan" contains 7 per cent. of aluminium, 70 of copper, and 23 of nickel.

Commercial magnalium always contains silicon, iron, and copper. For analysis, 1 gram of shavings is treated with Otis-Handy's acid mixture (compare *Berg.-Hüttenm. Zeit.*, 1897, 54) and the silicon estimated in the residue. The copper is precipitated by hydrogen sulphide. The iron is estimated volumetrically in a portion of the filtrate and the iron and aluminium precipitated together in another portion by means of ammonium acetate after oxidation with bromine water. The magnesium is precipitated by sodium phosphate. E. W. W.

Use of Potassium Periodate in the Detection of Manganese, Cobalt, and Zinc. STANLEY R. BENEDICT (*Amer. Chem. J.*, 1905, 34, 581—585).—When a few drops of *N*/10 solution of potassium periodate are added to a solution of a manganous salt, a red precipitate is formed or, if only a very small amount of manganese is present, a red coloration is produced. In a neutral solution, the precipitate retains its colour, but in presence of ammonia it rapidly becomes brown or black. The red coloration is produced even in a *N*/10,000 solution of manganous chloride.

Solutions of zinc salts yield a white precipitate with the reagent. In presence of ammonium chloride and ammonium hydroxide, precipitation does not take place in the cold unless the solution contains a large quantity of zinc, in which case a portion of it is precipitated. On boiling, however, the whole of the zinc is precipitated.

The following method is recommended for the detection and separation of manganese and zinc. The solution is treated with ammonium chloride and ammonium hydroxide and a drop of *N*/10 potassium periodate is added to a small portion of the solution, when the production of a pink or red coloration indicates the presence of manganese. If manganese is found to be present, it is completely precipitated by treating the solution with sodium phosphate. The

solution is filtered and the filtrate is tested for zinc with potassium periodate, potassium ferrocyanide, or hydrogen sulphide.

Periodates can be detected in presence of iodates by the addition of manganous chloride to the solution which has been previously treated with ammonium chloride and ammonium hydroxide; iodates give neither a precipitate nor a coloration under these conditions.

When pure nickel solutions are treated with the reagent, a light green precipitate is formed which, on boiling, becomes faintly grey in colour. Cobalt solutions, under similar conditions, yield a dark brown precipitate which, on further addition of the reagent, becomes green in colour and, when heated, dissolves to form a greenish-black solution.

The detection of cobalt in solutions of nickel salts can be accomplished as follows. To about 2—3 c.c. of the solution of $N/2$ — $2N$ strength, 1 c.c. of $N/10$ potassium periodate is added. If the precipitate produced is light green, cobalt is not present to the extent of more than 1 per cent. The solution is now heated to boiling; if cobalt is absent, the colour of the precipitate changes very slightly, but if present, the precipitate becomes olive-green, the depth of colour depending on the amount of cobalt. If more than 1 per cent. of cobalt is present, the precipitate shows a brown or olive-green tint in the cold. This test is very trustworthy and is capable of detecting 0.1 per cent. of cobalt in solutions of nickel salts. E. G.

Absolute Desiccation of Vegetable Substances. LÉON MAQUENNE (*Compt. rend.*, 1905, 141, 609—612).—The constant weight of vegetable substances, and probably of many mineral and organic compounds, after being heated for some time in an oven in ordinary air cannot be considered as a criterion of perfect dryness. Ordinary ovens should be absolutely proscribed in the case of such substances as starch, flours, and entire grain. These can be completely dried by heating for one hour at 120° and two hours at 100° in a current of dry air. N. H. J. M.

Chemical and Physical Methods for the Analysis of Pure Dilute Aqueous Solutions of Glycerol. HUGO HENKEL and A. W. ROTH (*Zeit. angew. Chem.*, 1905, 18, 1936—1941).—A review of the more important chemical and physical processes for the estimation of glycerol in its dilute aqueous solutions.

In the absence of foreign matter, the process to be recommended is the one proposed by Plancher (*Abstr.*, 1888, 1345), namely, oxidation with sulphuric acid and solid potassium permanganate and absorption of the dried carbon dioxide generated in a weighed soda-lime tube.

L. DE K.

Inhibition of Nylander's Sugar Reaction by the Presence of Mercury and Chloroform in the Urine. HEINRICH BECHHOLD (*Zeit. physiol. Chem.*, 1905, 46, 371—375).—Small quantities of mercury salts added to the urine, or present there as a result of the administration of mercury as a drug, prevent or lessen the intensity of the Nylander sugar reaction. Albumin, albumoses, and chloroform act in a similar way. W. D. H.

Apparatus and Methods for the Investigation of Raw Sugar, Fuels, and Beet Seeds. O. SCHREFELD (*Zeit. Ver. deut. Zuckerind.*, 1905, 1005—1048).—The author describes in detail the apparatus and methods used in the "Institut für Zucker-Industrie" of Berlin for the following determinations. (1) Polarisation, invert sugar, water and ash of raw sugars. (2) Calorific value of fuels. (3) Foreign matter, water, and germinative power of beet seeds. T. H. P.

Estimation of Sugar in Sugar-beets. AXEL TH. HÖGLUND (*Zeit. Ver. deut. Zuckerind.*, 1905, 1048—1058).—The author finds that, on filtering alcoholic solutions containing sugar, the first portions of the filtrate give lower polarimetric readings than those obtained later. This is shown to be due to the action of the filter paper, the loss in polarisation being nearly proportional to the amount of filter paper employed, no matter whether this has been specially dried or not. After a certain amount of the sugar solution has passed through the filter, the polarisation attains a constant value, which is, however, less than it should be where large quantities of filter paper have been used. Wood cellulose exhibits a behaviour similar to that of cotton cellulose.

Loss of sugar also takes place when the sugar-content of beets is estimated by the digestion process, the sugar being here absorbed by the cellulose of the beets. Although such loss does not occur in every case and to an appreciable extent, the author's observations indicate that, in the digestion of beets which are poor in juice or otherwise abnormal, the loss of sugar amounts to about 0.2 per cent.

T. H. P.

Estimation of Homogentisic Acid in Urine. ARCHIBALD E. GARROD and WILLIAM H. HURTLEY (*J. Physiol.*, 1905, 33, 206—210).—In estimating homogentisic acid in urine by Wolkoff and Baumann's method, the ammonia used should be in 8 per cent. solution. With 3 per cent. ammonia, the reduction is not complete in five minutes. Care should be taken to avoid the addition of too much hydrochloric acid, as excess masks the end-reaction. The correction for uric acid suggested by C. T. Mörner is as adequate as any general correction can be for so uncertain a quantity.

W. D. H.

The "Aldehyde" Value of Milk. R. STEINEGGER (*Zeit. Nahr. Genussm.*, 1905, 10, 659—671).—The natural acidity of milk is at once increased by the addition of formaldehyde, the increase reaching a maximum with the addition of 1.8 per cent. of formaldehyde or about 5 per cent. of the ordinary formalin (40 per cent.) solution. The difference between the original acidity of the milk and the acidity after the addition of 5 or 6 per cent. of formaldehyde solution is termed by the author the "aldehyde" value of the milk, the acidity of the formaldehyde solution itself being allowed for. For normal milks, this value (expressed in Soxhlet-Henkel degrees) varies from 5.8 to 8.5. For colostrum, the value may be as high as 17.3, but decreases as the milk becomes normal. The phenomenon is not due to the action of an oxidising ferment, as the increase is equally

marked in the case of boiled milk, but, as the aldehyde value varies with the amount of proteids contained in the milk, is undoubtedly caused by chemical reaction between the formaldehyde and the proteids. It is proposed to employ the aldehyde value as a means of detecting added water in milk, the value being lowered as the proteids decrease in percentage. The value is not, however, affected by abstraction of fat from the milk.

W. P. S.

Sichler's Sinacid Butyrometer. LOTTERHOS (*Zeit. Nahr. Genussm.*, 1905, 10, 596—599).—The author considers this process to be as rapid and trustworthy as Gerber's process, and shows that results which agree may be obtained in estimations of fat in full milk, skim milk, and cream. The details of the modification of the process used are: 10 c.c. of the salt solution (containing 15 per cent. of trisodium phosphate and 1 per cent. of trisodium citrate), 10 c.c. of milk, and 1 c.c. of isobutyl alcohol are placed in the butyrometer tube and well mixed. The tube and its contents are then heated to a temperature of 75° to 90°, again shaken, and subjected to centrifugal action for one minute. The reading is taken at a temperature of 70°.

W. P. S.

Sinacid Butyrometer and its use for Sheep's, Goats', and Cows' Milk. CARL BEGER (*Milchw. Zentr.*, 1905, 1, 547—551).—The results of a number of estimations of fat in sheep's, goats', and cows' milk are given, showing that by this process differences of from 0 to ± 0.45 in the percentage of fat may be obtained. The author considers that even where trustworthy results are obtainable the method offers no advantages over other centrifugal methods.

W. P. S.

Dika Fat. JULIUS LEWKOWITSCH (*Analyst*, 1905, 30, 394—395).—This fat is obtained from the seed kernels of various kinds of *Irvingia*, trees indigenous to the West Coast of Africa, from Sierra Leone to Gaboon. A sample of the fat, extracted by the author himself from the seeds, gave the following analytical figures: sp. gr., 0.9140 at 40°/40°; melting point, 38.9°; saponification number, 244.5; iodine number, 5.2; Reichert-Wollny number, 0.42; unsaponifiable matter, 0.73 per cent. Stearic acid was not present, and as Oudemans has shown that palmitic acid is also absent, the fat may be taken as consisting of myristin and laurin with a small quantity of olein.

W. P. S.

Foreign Fats and Oils. AUGUST SCHROEDER (*Arch. Pharm.*, 1905, 243, 628—640).—The results of the examination of several fats and oils are tabulated below; the columns of the table contain in succession: (a) saponification number, (b) iodine number, (c) Reichert-Meissl number, (d) Hehner number, (e) acid number (when two numbers are given, the first refers to the oil when newly extracted, the second after it has been kept for a time), (f) acetyl number, (g) percentage of glycerol, (h) percentage of non-saponifiable matter.

	a.	b.	c.	d.	e.		f, Ac No.	g, per cent.	h, per cent.
I.	268.2	2.28	1.47	76.1	3.35	8.82	—	13.03	1.44
II.	159.6	64.2	1.71	94.9	27.4	69.2	—	8.67	16.93
III.	198.2	127.8	117.5	—	95.1	57.4	27.9	9.49	0.71
IV.	193.8	81.9	78.4	6.43	85.8	37.9	44.5	8.3	12.78

I. Fat from the seeds of *Lepidadenia Wightiana*, from Java (*Litsæa sebifera*, *Cylicodaphne sebifera*, *Tetranthera calophylla*), known as Tangkala fat. This melted at 46° and had sp. gr. 0.8734 at 41°; it appeared to contain: laurin, 96.0 per cent.; olein, 2.6.

II. Oil from the seeds of *Strychnos nux vomica* (compare Harvey and Wilkes, *J. Soc. Chem. Ind.*, 1905, 24, 718). The oil had the sp. gr. 0.8826 at 20°; it appeared to contain olein, 74.5 per cent., solid glycerides, 8.6 (arachate and palmitate, with perhaps a little butyrate and decoate).

III. Oil from the seeds of the caoutchouc tree, *Hevea brasiliensis*, from Para. The oil had the sp. gr. 0.9293 at 20°; it appeared to contain palmitin with a little stearin, and glycerides of unsaturated acids which could not be identified.

IV. Oil from the root of *Polygala Senega*. The oil had the sp. gr. 0.9616 at 18°; it appeared to contain olein, 79.3 per cent., palmitin (with a little valerin), 7.9. C. F. B.

Detection of Formaldehyde. CARL GOLDSCHMIDT (*J. pr. Chem.*, 1905, [ii], 72, 536. Compare Abstr., 1905, ii, 867).—A résumé of some methods which have been proposed for the detection of formaldehyde (Abstr., 1898, i, 450; Trillat, Abstr., 1893, ii, 439; Lebbin, Abstr., 1897, ii, 606; Clowes and Tollens, Abstr., 1900, ii, 56; Pilhashy, *ibid.*, 453). Pyridine and quinoline bases are readily soluble in 30—40 per cent., but are insoluble in 25 per cent. formaldehyde solution. G. Y.

Indirect Estimation of Aldehydes in Oil of Lemons. ENRICO BERTÉ (*Gazzetta*, 1905, 35, ii, 437—450).—This method is based on the change in the rotation of the oil of lemons produced by removal from it of the aldehydes by means of potassium hydrogen sulphite solution, and is carried out as follows. To 10 c.c. of the oil, contained in an Erlenmeyer flask of about 250 c.c. capacity, are added 50 c.c. of saturated potassium hydrogen sulphite solution, the flask being then closed by a stopper through which passes a glass tube 40—45 cm. in length. The mixture is shaken so as to form an emulsion and is then heated on a water-bath for ten minutes, the flask being frequently shaken and care being taken not to heat it excessively. It is next allowed to cool completely and is then subjected to further heating with continuous agitation for five minutes. After cooling, the contents of the flask are introduced into a 100 c.c. tapped separating funnel, the yellow lower layer of oil being then separated, washed twice with a little distilled water, filtered in presence of a small quantity of anhydrous sodium sulphate and, when quite clear, read in the polarimeter. If the reading thus obtained is *A* and the initial reading of the oil, before treatment with the sulphite solution, *a*, the per-

centage, C , of aldehydes originally present in the oil is given by : $C = 100 (A - a)/A$. The method is found to give good results.

T. H. P.

Estimation of Vanillin. JOSEF HANUS (*Zeit. Nahr. Genussm.*, 1905, 10, 585—591).—Aqueous solutions of vanillin are precipitated quantitatively by *m*-nitrobenzoylhydrazide, the presence of acetanilide, benzoic acid, sugar, and salicylic acid having no influence on the estimation. For the estimation of vanillin in vanilla, 3 grams of the latter, in powder, are extracted for three hours with ether. The ethereal solution is evaporated, the residue is redissolved in a small quantity of ether, the solution filtered, again evaporated, and the residue heated for some time with 50 c.c. of water at a temperature of 60°. The emulsion thus obtained is then precipitated by the addition of 0.2 gram of *m*-nitrobenzoylhydrazide dissolved in 10 c.c. of water. The mixture is kept on the water-bath for thirty minutes and then set aside for twenty-four hours. The whole is now extracted three times with light petroleum, the extracts being poured through a Gooch's filter, and finally the precipitate is also brought on to the filter. The precipitate is washed with water, then with light petroleum, dried at 100°, and weighed. By multiplying the weight of precipitate obtained by 0.4829, the quantity of vanillin is found.

W. P. S.

Tests for the Purity of Hexamethylenetetramine. ALFRED WÖHLK (*Zeit. anal. Chem.*, 1905, 44, 765—766).—Unless ammonium salts are present, hexamethylenetetramine gives no coloration with Nessler's reagent either in the cold or when heated. The presence of paraformaldehyde can be detected similarly, since a trace of the latter reduces Nessler's reagent on warming.

W. P. S.

Detection of Choline by the Polarisation Microscope. JULIUS DONATH (*J. Physiol.*, 1905, 33, 211—219).—The double refraction and chromatic polarisation exhibited by crystals of choline platinichloride may be used as a delicate test for distinguishing this compound from potassium and ammonium platinichlorides and for detecting small quantities of choline in liquids such as the cerebrospinal fluid. The results confirm those obtained previously by other methods.

W. D. H.

Detection of Choline in Physiological Fluids. OTTO ROSENHEIM (*J. Physiol.*, 1905, 33, 220—224).—The importance of the presence of choline in cerebrospinal fluid and blood in cases of degenerative nervous diseases, as shown by Halliburton and Mott, Donath, and others, renders necessary some simple test which can be applied to the small quantities which are alone available as a rule. The best test appears to be to prepare the platinichloride and add to it a solution of iodine in potassium iodide; the crystals rapidly dissolve, and crystals of choline periodide take their place; as the iodine evaporates, the latter disintegrate into oily droplets. Crystals of other platinichlorides liable to be mistaken for the choline compound are unaffected by the iodine solution. Other tests are: (1) the addition of alloxan gives a rose-violet colour, which is changed to bluish-violet by sodium or potassium

hydroxide, and discharged by mineral acids; and (2) the addition of potassium bismuthiodide produces a brick-red, amorphous precipitate.

W. D. H.

Estimation of Indole. CHRISTIAN A. HERTER and M. LOUISE FOSTER (*J. Biol. Chem. New York*, 1906, 1, 257—262).—The method is based on the colour reaction which follows the condensation of indole with sodium β -naphthaquinonesulphonate. There is a rough parallelism between the intensity of the indician reaction of the urine and the quantity of indole in the fæces.

W. D. H.

Estimation of Tannin in Wine. LUDWIG KRÁMSKY (*Zeit. anal. Chem.*, 1905, 44, 756—765).—From 50 to 100 c.c. of the wine are rendered alkaline with ammonia and precipitated with a solution of zinc hydroxide. The latter reagent is prepared by dissolving 25 grams of zinc sulphate in water, adding sufficient ammonia to redissolve the precipitate formed, then 300 c.c. of ammonia, and finally water to make the volume up to 1 litre. The precipitate of zinc tannate is stirred until it coagulates and settles. Three hundred c.c. of hot water are added, and the precipitate collected on a weighed filter, washed with dilute ammonia, dried at 100°, and weighed. The filter and precipitate are now ignited, and the weight of zinc oxide obtained is subtracted from the total weight, the difference giving the amount of tannin. Gallic acid is not precipitated by the above reagent, and the ordinary constituents of wine have no influence on the estimation.

W. P. S.

Estimation of Tannin by means of Strychnine. SAMUEL R. TROTMAN and JOHN E. HACKFORD (*J. Soc. Chem. Ind.*, 1905, 24, 1096—1100).—About 2·5 grams of material (sumach, for instance) are extracted in a Soxhlet tube with alcohol. The solution is concentrated to 50 c.c., then diluted with water to 100 c.c., and the resins, &c., which are precipitated, filtered off. Twenty-five c.c. of the filtrate are evaporated to obtain the total water-soluble matters, and another 25 c.c. are treated as follows: after introduction into a 250 c.c. flask and adding some water, a solution is added prepared by dissolving 0·25 gram of strychnine in 50 c.c. of alcohol and diluting with 50 c.c. of water. After diluting to the mark, the whole is well shaken and the precipitate collected at the suction-pump on a weighed asbestos filter. The strychnine tannate is finally dried at 60° in a vacuum. One hundred parts = 49·1 parts of tannin.

L. DE K.

Value of the Spectrum of Hæmochromogen. ANGELO DE DOMINICIS (*Chem. Centr.*, 1905, ii, 1195; from *Berl. klin. Woch.*, 42, 1219—1220).—A particle of the dried blood is rubbed with a drop of pyridine and a drop of ammonium sulphide added. In this manner, there is obtained the purplish-red colour reaction of hæmochromogen, hæmochromogen crystals, and the spectrum of hæmochromogen.

N. H. J. M.

Detection of Bile Pigments in Urine. LÉON GRIMBERT (*J. Pharm. Chim.*, 1905, [vi], 22, 487—492).—The author suggests the

following modification of the methods of Hammarsten (compare Abstr., 1900, ii, 637) and of Salkowski (compare *J. Pharm. Chim.*, 1894, [v], 30, 125) for the detection of bile pigments in urine. A mixture of 10 c.c. of the urine and 5 c.c. of a 10 per cent. solution of barium chloride is centrifugalised, the precipitate of the barium sulphate, phosphate, and possibly bilirubin compound, taken up with 4 c.c. of alcohol containing 5 per cent. of its volume of hydrochloric acid, is boiled on the water-bath for a minute, and the precipitate allowed to settle. If the supernatant liquid is colourless, the urine is free from bile pigments; if it is coloured bluish-green or deep green, bile pigments are present; if, however, it has a brown colour, two drops of hydrogen peroxide (10 vols.) are added and the heating repeated. This will oxidise to biliverdin any bilirubin which may have escaped oxidation by the alcoholic hydrogen chloride, and the characteristic green colour will appear.

M. A. W.

Valuation of Barley. C. BLEISCH and P. REGENSBURGER (*Chem. Centr.*, 1905, ii, 1195—1196; from *Zeit. ges. Brauw.*, 28, 625—631).—The examination of about eighty barleys (mostly Bavarian) showed that with the increase in proteid the amount of extract diminishes (from 78.5 to 74.8 per cent.). The malt extract curve is not completely parallel to the barley extract curve; between 10.0 and 10.5 per cent. of proteid, in a large number of malts, there is a rise. The maximum in both cases is with about 9 per cent. of proteid.

The amount of spelt seems to have a certain importance in Bavarian (although perhaps not for Silesian) varieties.

The loss of proteid in malting is greater in barleys rich in proteid than in those with less proteid.

N. H. J. M.

Relation of the Amount of Nitrogen to the Character of Barley. EUGEN PRIOR (*Chem. Centr.*, 1905, ii, 1390; from *Allgem. Zeit. Bierbrau. Malzfabr.*, 1905, and *Zeit. ges. Brauw.*, 28, 684—685).—The determination of the apparent steeliness of barley by softening and then drying (Grönlund) is preferable to the estimation in the original barley of the amounts of starchy, steely, and intermediate grains. The results are expressed by the formula

$$(M_1 + M)100/(100 - M) + M$$

("Auflösungsgrad"), in which M is the number of starchy grains in 100 of the original barley and M the number in 100 of softened and afterwards dried barley. Whilst single results showed no relation to the amount of nitrogen, average results showed that this relation diminished as the nitrogen increased. The uncertainty of the indications is attributed to differences in the character of the nitrogen compounds.

N. H. J. M.

Relations between the Amounts of Nitrogen and the Character of Austrian Barleys to the Yield of Extract and to the Friability of the Malt. EUGEN PRIOR (*Chem. Centr.*, 1905, ii, 1390—1391; from *Allgem. Zeit. Bierbrau. Malzfabr.*, 1905).—The amount of proteid in the barley agreed with that of the malt only in

twenty-three out of forty-eight cases, owing to the varying amounts of water-soluble nitrogenous compounds in the barley and differences in the manner and duration of softening. Barleys with 10—11 per cent. of proteid gave results similar to those with 9—10 per cent. It would seem, therefore, that only those with more than 11 per cent. yield inferior malt.

Evidence was obtained that an intimate relation exists between the "Auflösungsgrad" (preceding abstract) of the barley, the friability of the malt, and the yield of extract. The rule applied by Haase to Silesian barley, that the extract diminishes with an increase in the proteids, does not hold good in the case of Austrian barley.

N. H. J. M.

Estimation of Lecithins. WALDEMAR KOCH and HERBERT S. WOODS (*J. Biol. Chem. New York*, 1906, 1, 203—212).—Some modifications of Koch's former methods for the separation and estimation of lecithins and kephalins are proposed, and the amounts of these two classes of substances in most of the body tissues and some foods (such as bread, eggs, and milk) are given in tabular form. The numbers are usually under 1 per cent., and frequently the kephalins are more abundant than the lecithins.

W. D. H.

Some Methods of forming Hydrazines and their Influence on Biochemical Analysis. NAZARENO TARUGI (*Chem. Centr.*, 1905, ii, 1638—1639; from *Boll. Chim. Farm.*, 44, 589—595. Compare Schestakoff, Abstr., 1905, i, 332).—A sample of fresh urine was found to be incapable of reducing Fehling's solution, and did not acquire this property until it was at least two hours old. After repeatedly filtering, however, it gave a blue coloration with tincture of guaiacum although it was completely free from both albumin and pus; after heating at 70° for five seconds, it ceased to give the reaction, but the coloration was again formed when hydrogen peroxide was added. The filtered urine after boiling did not give the blue coloration either directly or when hydrogen peroxide was added. The abnormal behaviour of the urine is probably due to the presence of an oxydase (compare Abstr., 1903, ii, 460; 1904, ii, 220) which attacks the carbamide forming carbon dioxide and hydrazone. In support of this hypothesis, experiments have shown that by the action of oxidising agents (hypochlorites, persulphates) and vegetable and animal extracts containing oxydase on Haga's and Sachsse and Knapp's solutions, reducing actions also take place which are probably caused by the hydrazine that has been formed by oxidation of carbamide. The possibility of the occurrence of hydrazine is of importance in reference to biochemical analysis.

E. W. W.

General and Physical Chemistry

Periodic Relation between the Atomic Weights and the Index of Refraction. F. L. BISHOP (*Amer. Chem. J.*, 1906, 35, 84—86).—A table is given of the elements arranged in order of increasing atomic weight, together with their atomic weights and refractive indices. A curve is constructed, in which the atomic weights are plotted as abscissæ and the refractive indices as ordinates. In this way, a periodic relation between the atomic weight and index of refraction is made apparent. The elements form certain well-defined groups, in which the minima are Na, Cu, Ag, and Au. The periodicity is most evident in the series from C to Cl, as in this series the refractive indices of all the elements are available. E. G.

Flame Spectrum of Mercury. CHARLES DE WATTEVILLE (*Compt. rend.*, 1906, 142, 269—270).—When the spray from a solution of mercuric acetate, cyanide, or nitrate is injected into the gas to be burned, the flame spectrum of the metal thus obtained consists of one well-marked line, 2536·72 (compare Hartley and Ramage, *Abstr.*, 1902, ii, 189; Gouy, *Abstr.*, 1877, ii, 105), and in this respect mercury resembles the other metals (magnesium, calcium, zinc, strontium, cadmium, and barium) of the second group in the periodic classification (compare Ramage, *Abstr.*, 1902, ii, 545; Watteville, *Abstr.*, 1905, ii, 2). The three points obtained for magnesium, zinc, and cadmium by plotting the atomic weights of the metals against the wave-lengths of the characteristic line of their spectra lie almost on a straight line, the prolongation of which passes through a point which requires the wave-length 3650·31 for the characteristic ray of mercury, the line which is very prominent in the arc spectrum of the metal.

M. A. W.

[**Mutarotation of Sugars.**] CHARLES TANRET (*Zeit. physikal. Chem.*, 1905, 53, 692).—Jungius in his recent paper (*Abstr.*, 1905, i, 573) has overlooked the author's latest work (*ibid.*, i, 327).

J. C. P.

Solarisation in Silver Bromide Films. HERMAN WEISZ (*Zeit. physikal. Chem.*, 1906, 54, 305—352).—The author, after reviewing recent work bearing on the nature of the latent image in silver bromide and chloride (see, for example, Luther, *Abstr.*, 1900, ii, 181, 253; Abegg, *Abstr.*, 1900, ii, 253; 1901, ii, 217; Baur, *Abstr.*, 1904, ii, 4), concludes that it consists of a solid solution of silver subhaloid and (possibly) silver in silver haloid. This solid solution contains but little silver subhaloid or silver, and is very stable towards oxidising and reducing agents. It appears that every substance capable of forming a solid solution with silver can act as a nucleus for both chemical and physical development; thus, gold, platinum, rhodium, iridium, and silver sulphide can act as nuclei for development.

The latent image is developable probably because the solid solution referred to above is able to form solid solutions with silver and silver subhaloid. The silver haloid of the sensitive film is reduced by the developer to silver and to silver subhaloid.

The phenomenon of solarisation has been observed in the case of silver bromide films deposited on glass without the aid of any binding medium such as gelatin. It is shown that solarisation is due neither to conversion of the silver bromide of the film into a modification which is reduced only with difficulty nor to tanning of the gelatin preventing diffusion of the developer.

A method is described whereby the tanning of gelatin in different plates may be detected and compared. J. C. P.

Cathodic Phosphorescence of Europium. GEORGES URBAIN (*Compt. rend.*, 1906, 142, 205—207. Compare Abstr., 1904, ii, 340; 1905, ii, 250, 458, 711; this vol., ii, 28).—Pure europium oxide does not give a phosphorescent spectrum, but when diluted with lime even in the proportion of $1\text{Eu}_2\text{O}_3 : 99\text{CaO}$ it gives a red phosphorescence, and similar results are obtained with the mixtures of europium and gadolinium oxides forming the intermediate fractions in the separation of the two elements. The fractions rich in europium give a red, and those rich in gadolinium give a white, phosphorescence, the spectra of the consecutive fractions changing gradually just as if europium were a mixture of two phosphorescent earths already beginning to separate. This is, however, not necessarily the explanation, for if a specimen of pure europium oxide be diluted with increasing quantities of pure gadolinium oxide, the spectra of the mixtures show a similar series of changes, and similar results are also obtained with mixtures of pure europium oxide and alumina or lime. M. A. W.

Absorption of α -Rays. R. K. McCLUNG (*Phil. Mag.*, 1906, [vi], 11, 131—142).—A uniform and homogeneous source of α -rays is obtained by exposing a thin wire in a vessel containing the emanation from radium; the deposit on the wire contains three products, radium *A*, *B*, and *C*, but the first disappears in a very short time and the second gives out no rays. A wire prepared in the foregoing manner was placed at the bottom of a narrow hole in the middle of a brass block, and the well-defined cone of rays thus obtained was directed towards wire gauze kept at a constant potential and placed opposite to a zinc plate, which, in its turn, was connected to one pair of quadrants of an electrometer. From the rate of leak observed for different positions of the radiating material, it was possible to study the extent to which the α -rays are absorbed by their passage through air. Allowance was duly made for the gradual decay of the activity.

When the source of radiation is at first quite close to the gauze, and is then gradually moved away, the ionisation produced gradually increases, and at a distance of about 5.8 cm. reaches a maximum; it then diminishes very rapidly until at a distance of 6.8 cm. it ceases altogether. The range in air over which the α -ray can produce ionisation is therefore about 6.8 cm., in good agreement with the value 6.7 cm. obtained by Bragg and Kleeman (Abstr., 1905, 4, 5). Almost

the same value too has been found by Rutherford (Abstr., 1905, ii, 495) in his investigation of the distance at which the photographic and phosphorescent actions of the α -rays cease.

When thin aluminium foil is interposed between the source of α -radiation and the gauze, the total effective range of the α -rays is shortened, and the maximum ionisation occurs at a point nearer the gauze. From a comparison of the thickness of the aluminium foil and the extent to which the total range of the α -rays is shortened, it is calculated that the thickness of air equivalent to one layer of the aluminium foil (0.00031 cm. thick) is 0.5 cm. Rutherford (*loc. cit.*), using the photographic and phosphorescent screen methods, found that 0.00031 cm. of aluminium was equivalent in absorptive power to 0.54 cm. of air.

J. C. P.

Some Properties of the α -Rays from Radium. ERNEST RUTHERFORD (*Phil. Mag.*, 1906, [vi], 11, 166—176).—The author deals with the criticisms contained in a recent paper by Becquerel (Abstr., 1905, ii, 665; compare also 1903, ii, 256, 257, 402, 523; 1904, ii, 6), who believes that the α -rays from radium are homogeneous, that the α -particles all escape into the air with the same velocity, that this velocity is not altered by their passage through matter, and that the mass of the α -particle somehow increases in its passage through air, the last statement being the explanation of the decreasing curvature of the path of the rays in their passage through air.

The author reviews the experimental evidence and the various interpretations suggested by Bragg and Kleemann (Abstr., 1905, ii, 4, 5, 791), Becquerel (*loc. cit.*), and himself (Abstr., 1905, ii, 495), and concludes that the rays from radium in radioactive equilibrium are complex, that they consist of α -particles projected with different velocities, and that these velocities decrease as the particles pass through air or aluminium. The two phenomena observed by Becquerel, namely, (1) the absence of increased deflection of the rays from a thick layer of radium after passing through aluminium, (2) the decreasing curvature of the path of the rays in air, are both necessary consequences of the complexity of the rays. There is evidence also of a distinct scattering of the rays from radium C in their passage through air.

J. C. P.

Character of α - and γ -Rays. OTTO WIGGER (*Jahrb. Radioakt. Elektronik.*, 1905, 2, 391—433).—In order to obtain α -rays of homogeneous character, radiotellurium and polonium were used as source of the radiation instead of radium, which gives rise to several types of α -rays. Evidence of the nature of the α -rays has been obtained by a study of their absorption. Whereas the total absorption coefficient of a bundle of rays of light of different wave-lengths decreases with increasing thickness of the absorbing layer, the opposite is the case with rays consisting of small material particles. In consequence of collisions in the absorbing medium, an initially homogeneous bundle of rays becomes heterogeneous, the mean energy (velocity) becomes smaller, and since the absorption increases as the velocity diminishes, the absorption-coefficient should increase with the

thickness of the layer traversed. The experimental data indicate that the absorption-coefficient of the α -rays of radiotellurium and polonium increases with the thickness of the absorbing layer, and the material nature of the rays is established. Experiments on the leakage between a radiotellurium or polonium rod and a copper cylinder, both well insulated and contained in a highly exhausted vessel, indicate that these substances emit negatively charged particles of low velocity as well as positively charged α -rays. The β -rays are deviated by a magnetic field, but Becquerel's observation that the α -rays of polonium are deviated is not confirmed by the author's experiments on radiotellurium. Using the photographic method, no evidence of deviation of the α -rays could be obtained, and the conclusion is reached that these cannot be identical with the α -rays of radium.

In order to obtain information on the question as to whether the γ -rays of radium are rapidly moving β -rays or Röntgen rays, the author has examined by the ionisation method the absorption of these rays by plates of lead, employing much thicker layers of the metals than were used in the previous experiments of Rutherford and McClelland. The absorption-coefficient decreases at first with increasing thickness of the lead plate, but attains a constant value for a thickness of 1.6 cm. This can only be explained on the assumption that the γ -rays consist of Röntgen rays.

When the γ -rays traverse any material, they give rise to a secondary radiation which is also capable of ionising gases and thus interferes with the effect due to the γ -rays. The amount of this secondary radiation depends on the material traversed by the rays, and in the experiments on the absorption power of different metals the effect was eliminated by interposing the substance between the radium preparation and a lead plate 2.8 cm. thick. This plate served to absorb the secondary radiation, and was placed at the entrance to the ionisation chamber. The absorption-coefficient of the penetrating γ -rays which enter the chamber in these circumstances is found to be strictly proportional to the density of the interposed material. The following values were obtained, K being the absorption-coefficient and d the density :

	Mercury.	Lead.	Copper.	Iron.	Zinc.	Aluminium.	Sulphur.
$K(\text{cm}^{-1})$	0.283	0.241	0.191	0.159	0.141	0.054	0.040
K/d	0.0208	0.0213	0.0226	0.0211	0.0201	0.0200	0.0202

These values for K are much smaller than those given by Rutherford and McClelland. A definite significance can only be ascribed to such numbers when the thickness of the medium traversed is indicated and the effect of secondary radiation is eliminated. H. M. D.

Ionisation produced in various Gases by the Secondary β - and γ -Rays of Radium. GOTTLIEB KUČERA (*Ann. Physik*, 1905, [iv], 18, 974—990).—The ionisation produced in a number of gases by secondary radiation from various solid substances is found to be the same for all the gases. The intensity of the secondary radiation from those of the solid substances which are elements falls off in general with increase of the atomic weight. Comparison of the author's results with those of Strutt (*Proc. Roy. Soc.*, 1903, 72, 208) shows that there

is complete agreement between the relative ionisation due to secondary radiation and that due to the β -rays of radium. Certain abnormal phenomena observed in the case of freshly-prepared gases are attributed to the presence of very sluggish ions which are only gradually eliminated.

J. C. P.

Heating Effects produced by Röntgen Rays in different Metals and their Relation to the Question of Change in the Atom. H. A. BUMSTEAD (*Phil. Mag.*, 1906, [vi], 11, 292—317).—When metals and other substances are exposed to Röntgen rays, a complex secondary radiation is produced, which is, to some extent at least, of different character from the primary radiation. The secondary radiation may arise from atomic disintegration produced by the Röntgen rays, in which case the law of the conservation of energy will not apply, or may be due to other causes, when the law in question may be expected to hold. To test this point, thin strips of lead and zinc, covered on both sides with aluminium foil so as to have the same emissive power, were exposed alternately to the rays, and the radiation from the two compared by reading the deflections on a radiometer with aluminium vanes; since the secondary radiation is to a great extent absorbed by the metals, the readings will be a measure of the amounts of heat generated in the strips. When the conditions were such that the rays were equally absorbed in the two strips, it was found that approximately twice as much energy was generated in the lead as in the zinc. The result is best accounted for on the view that Röntgen rays bring about atomic disintegration; the energy thus liberated probably forms the greater part of the energy which appears when the rays are absorbed by matter.

G. S.

***n*-Rays.** ÉLEUTHÈRE MASCART (*Compt. rend.*, 1906, 142, 122—124. Compare Blondlot, *Abstr.*, 1904, ii, 604; Bichat, *Abstr.*, 1904, ii, 531, 532, 641; Becquerel, *Abstr.*, 1904, ii, 602, 641, 642; Rothé, *Abstr.*, 1904, ii, 603; Gutton, *Abstr.*, 1904, ii, 603).—Details are given of a series of measurements of the position of points of maximum intensity in the spectrum produced by passing the *n*-rays from a Nernst lamp through an aluminium prism. For this purpose, a phosphorescent screen was mounted on the carriage of a dividing engine, and each of four independent observers (Blondlot, Gutton, Vartz, and Mascart) either recorded the position of the screen at points of maximum intensity whilst the carriage proceeded in one direction, or the carriage was arrested by the observer at such points whilst proceeding both up and down the scale, and the readings were taken by a second person. The results obtained by the latter method are appended:

Blondlot	{	→ 375·6	370·4	363·4	356·2
			← 375·3	370·3	363·4	356·2
Gutton	{	→ —	371·4	364·2	356·1
			← 374·8	367·4	361·3	356·6
Vartz	{	→ 374·9	369·8	364·6	357·6
			← 374·6	371·6	364·3	358·2
Mascart	{	→ —	372	—	356
			← 376·5	370	—	356

M. A. W.

Photographic Experiments on the Action of n -Rays on an Oscillating Spark. C. GUTTON (*Compt. rend.*, 1906, 142, 145—149).—Blondlot observed that when the primary spark of a Hertzian oscillator is subjected to the action of n -rays, the brightness of the secondary spark is diminished (*Rev. gén. Sci.*, 1905, 727). The author has obtained photographic confirmation of this observation by developing a photographic plate, one-half of which has been exposed for one minute to the action of the secondary spark of a Hertzian oscillator, and the other half similarly exposed, while the primary spark is subjected to the action of n -rays from a Nernst lamp; thirty-seven such photographs show that the brightness of the secondary spark is diminished by the action of n -rays on the primary spark. The original contains full details of the apparatus employed. M. A. W.

Relation between the Radioactivity and the Composition of Uranium Compounds. HERBERT N. MCCOY (*Phil. Mag.*, 1906, [vi], 11, 176—186. Compare Abstr., 1904, ii, 528; 1905, ii, 366).—The author's previous work showed that the total activity of 1 gram of pure uranium is 791 times that of 1 sq. cm. of a layer of the pure oxide U_3O_8 , sufficiently thick to be of maximum activity. The proof that this oxide was free from appreciable quantities of radium has now been obtained by starting with a uranium ore and continuing the processes of purification until no further change of activity occurred. The oxide U_3O_8 , obtained as a result of these processes, had practically the same activity as the pure oxide used previously, which was obtained by the ignition of uranium nitrate.

The oxide U_3O_8 may be used in preparing a standard of activity capable of being reproduced with an accuracy of a few tenths of 1 per cent. Ordinary uranium salts are treated successively with ammonium carbonate, ammonium sulphide, and barium chloride. Ammonium uranate is precipitated and converted into the oxide U_3O_8 by ignition in a current of oxygen. About 1 gram of the oxide is reduced to an impalpable powder by grinding in an agate mortar with some freshly-distilled chloroform. It is then stirred up with more chloroform and poured into a shallow metal dish about 7 cm. in diameter. Spontaneous evaporation of the chloroform then leaves a uniform adherent black film of the oxide. The total activity of 1 gram of uranium is 791 times the observed or surface activity of each sq. cm. of such a film.

The total activity of any uranium compound may be found also by comparing the activities of films of the compound of different thicknesses with the activity of a standard film of the oxide U_3O_8 , prepared as above, and then extrapolating to zero thickness. This method is shown to give good results in the case of pure uranium compounds, and has further been used to determine the total activity of samples of pitchblende, gummite, and carnotite. It is found that for the foregoing minerals the ratio k/P , where k is the total activity of unit-mass of the mineral and P is the weight of uranium in 1 gram of the mineral, is nearly constant and equal to 3280. This means that for equal content of uranium the ores are 4.15 times as active as the pure uranium com-

pounds. It is further estimated that radium is 3.3×10^6 to 4.25×10^6 times as active as uranium.

J. C. P.

Radioactivity of Uranyl Double Salts. WILLY MARCKWALD (*Ber.*, 1906, 39, 200—203. Compare Meyer and Wendel, *Abstr.*, 1904, ii, 130; Rimbach, *ibid.*, ii, 264).—The statement of Rimbach and Grewe that certain uranium compounds exhibit greater activity than uranium itself is inconsistent with Rutherford's theory. The author has therefore examined the behaviour of uranyl potassium nitrate, uranyl thallium nitrate, uranyl ethylenediamine nitrate and sulphate, and uranium nitrate, and finds that the intensity of the α -rays, measured by an electrometer, is the same in each case. In order to compare the intensity of the β -rays, flat, thin-walled glass flasks containing the salts were placed on opaque paper enclosing a photographic plate and masked with patterns of glass, lead, and aluminium foil; the behaviour of the five salts was almost the same. When the flasks are placed directly on the plate, the latter exhibits marked blackening due to the emission of light from the salts, particularly the uranyl potassium nitrate and the uranyl ethylenediamine nitrate, which by their pronounced fluorescence also differ from the other three.

C. S.

Diminution of the Radioactivity of Polonium with Time. [Madame] MARIE CURIE (*Compt. rend.*, 1906, 142, 273—276).—A specimen of poloniferous bismuth oxide (*Abstr.*, 1900, ii, 82), 250 times more active than uranium, was placed in a shallow, circular cavity in a metal disc and the radioactivity measured at stated intervals of time. The diminution in the intensity of the radiation is an exponential function of the time, and is expressed by the equation $I = I_0 e^{-at}$; the activity falls to half the original value in 140 days. The value of the constant a , which is characteristic of polonium, is 0.00495 when t is measured in days, and is identical with the corresponding constant (0.00497) found by Marckwald for radiotellurium (*Abstr.*, 1902, ii, 508; 1905, ii, 159, 623), a fact which establishes its identity with polonium, the first strongly radioactive element discovered by the author and Pierre Curie. The curve obtained by plotting the time against $\log I$ in the above experiment is a straight line, and parallel lines are obtained when plates of bismuth dipped in solutions of the chloride of radioactive bismuth are used instead of the poloniferous bismuth oxide (Marckwald, *Abstr.*, 1902, ii, 508) or when a similar plate is covered with a sheet of aluminium 0.01 mm. in thickness.

M. A. W.

Photoelectric Effect of Selenium. CAMILLO CARPINI (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 667—673).—At the temperature of liquid air, the photoelectric effect of selenium is detectable, but very slight. Bidwell's theory, according to which the action of light determines the formation of conducting selenides, is hence improbable. The author found that the photoelectric effects of two preparations of selenium were 0.32 and 0.247 respectively at about 8° and 0.07° at 96° , the temperature-coefficient being hence 0.003 and 0.002 in the two cases. The resistance-brightness curve for selenium varies according as the light-intensity is being raised or diminished.

T. H. P.

Decomposition of Carbon Dioxide by the Point Discharge. T. NODA and EMIL WARBURG (*Ann. Physik*, 1906, [iv], **19**, 1—13. Compare Warburg, *Abstr.*, 1904, ii, 24; Gray, *ibid.*, 25).—Brodie, using a Siemen tube, found (*Phil. Trans.*, 1874, **164**, 83) that carbon dioxide exposed to the action of the silent discharge was decomposed to the extent of 1.5—2.7 per cent., and that about 50 per cent. of the oxygen produced was ozonised. The authors, using a point discharge, find that the carbon dioxide is decomposed to the extent of 3 per cent., and that about 19 per cent. of the oxygen produced is ozonised.

The number of coulombs required to decompose a gram-equivalent of carbon dioxide is only 2610, which shows that the decomposition of this gas by the silent discharge is not an electrolytic process. It is shown also that of the electrical energy supplied only 1.1 per cent. is converted into chemical energy.

For a negative point discharge, it appears that the amount of decomposition depends only on the total electricity, not on the current strength. Further, the number (N) of coulombs per molecule of carbon dioxide decomposed increases as the density of the gas is diminished. It is found that N falls off as the temperature rises; but this result requires further experimental support. J. C. P.

Some Concentration Cells in Methyl and Ethyl Alcohols. J. HUNT WILSON (*Amer. Chem. J.*, 1906, **35**, 78—84).—Determinations have been made of the *E.M.F.* of some cells of the type $\text{Ag}-N/10$ alcoholic silver nitrate— $N/100$ alcoholic silver nitrate— Ag , at 25° and 0°. Solutions of silver nitrate of four different concentrations in methyl alcohol and of three different concentrations in ethyl alcohol were employed. The results are tabulated and compared with the values of the *E.M.F.* calculated from Nernst's formula. The agreement between the observed and calculated values is good in the case of the ethyl alcohol cells, but somewhat poor in that of the methyl alcohol cells. The results indicate that Nernst's formula is applicable to alcoholic as well as to aqueous solutions, but further experiments are required to confirm this conclusion. E. G.

Electrical Conductivity of Solutions of Compounds of Dimethylpyrone with Trichloroacetic Acid in Chloroform and Benzene. WLADIMIR A. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 875—881. Compare *Abstr.*, 1905, ii, 433).—The author finds that the two double compounds formed from dimethylpyrone and trichloroacetic acid have measurable conductivities, and are hence dissociated in benzene or chloroform solution. These results are in disagreement with those of Kahlenberg and Lincoln (*Abstr.*, 1899, ii, 397) and of Patten (*Abstr.*, 1903, ii, 417), who state that chloroform has no appreciable ionising power. T. H. P.

Relation between Electrolytic Dissociation and Dielectric Constant. EMIL BAUR (*Zeit. Elektrochem.*, 1905, **11**, 936—938).—In the partition of an electrolyte between two solvents, it is not unlikely that the ratio of the concentrations of the ions in the two solvents might be equal to the ratio of the cubes of the dielectric constants of

the solvents. The author attempts to test this by means of existing data without any conclusive result. T. E.

Cathodic Behaviour of Sulphur, Selenium, and Tellurium. ERICH MÜLLER and ROMUALD NOWAKOWSKI (*Zeit. Elektrochem.*, 1905, 11, 931—936. Compare this vol., ii, 18, and Le Blanc, this vol., ii, 67).—In 0.1*N* potassium hydroxide solution, selenium dissolves at the cathode with the valency 0.67 to 0.75, sulphur with the valency 0.57 to 0.89, and tellurium with valency about 0.9. The potentials at which solution begins (measured against the 0.1*N* calomel electrode) are sulphur 0.53 volt, selenium 0.804 volt, tellurium 1.07 volt.

T. E.

Oxidation and Reduction in the Electrolysis of Salts of Iron. Z. KARAOGLANOFF (*Zeit. Elektrochem.*, 1906, 12, 5—16. Compare Abstr., 1905, ii, 674).—The rate of reduction of a ferric salt by electrolysis depends on the rate at which ferric ions can be changed into ferrous ions at the electrode and on the rate at which ferric ions can diffuse into the layer of solution in contact with the electrode. In a solution which is not stirred, convection also occurs; owing to the changes of composition and density in the solution near the electrode, convection currents are produced which tend to keep up the concentration of the ferric ions at the electrode. The same considerations hold good for the oxidation of a solution of a ferrous salt.

By an application of Sand's method (Abstr., 1901, ii, 82), the author shows that the time t during which a current i must flow in order to diminish the concentration of the ferric or ferrous ions at the electrode to such a small value that hydrogen (or oxygen) is evolved in a solution of concentration c is given by the expression $i\sqrt{t} = k.c$. The constant k is proportional to the square root of the diffusion coefficient of the salt. This formula is shown to hold good for ferrous and ferric salts so long as the current is not too small. For very small currents, convection at the electrode suffices to maintain the concentration of the ferrous or ferric ions above the limit at which gas is evolved.

The potential of the electrode during the period in which the concentration of the iron salt is diminishing is also measured, and the curves obtained are found to have the general form required by the assumptions that the loss of ferric ions at the electrode is being replaced by diffusion and that the relation between the potential of the electrode and the concentration of the solution is given by Peters' formula (Abstr., 1898, ii, 419).

T. E.

Rate of Migration of Complex Ions. JAMES W. MCBAIN (*Zeit. Elektrochem.*, 1905, 11, 961—963).—A *résumé* of the methods which have been proposed for measuring the rate of migration of complex ions (Trans., 1904, 85, 1305, and Abstr., 1905, ii, 371).

T. E.

Physico-chemical Side of Organic Electrochemistry. WALTHER LÖB (*Zeit. Elektrochem.*, 1906, 12, 2—5).—General remarks on the

inter-connection of the physico-chemical and preparative aspects of organic chemistry.

T. E.

New Magneto-optical Properties of Colloidal Solutions of Ferric Hydroxide. A. COTTON and H. MOUTON (*Compt. rend.*, 1906, 142, 203—205).—The authors have previously shown (*Compt. rend.*, 1905, 141, 317, 349) that the property shown by certain colloidal solutions of ferric hydroxide of becoming doubly refracting (positive or negative) when placed in a uniform magnetic field and illuminated by a ray of light perpendicular to the field appears to be associated with the size and not with the nature of the particles, for the double refraction is greatly increased by heating the solutions, whereby the size of the particles is augmented. Similar results were obtained with a solution containing minute crystals of calcium carbonate in suspension.

In the present paper, it is shown that the matter in suspension in these solutions has a negative magnetic rotation, greater in extent and opposite in sign to that of water, so that when such a concentrated solution is diluted the magnetic rotation, initially negative, becomes zero and finally positive.

The magnetic rotation of these solutions does not vary directly with the strength of the magnetic field (law of Verdet), but increases rapidly at first and then more slowly.

The effects produced by a magnetic field on certain colloidal solutions are probably due to the magnetism and orientation of the particles in suspension, for if gelatin is added to one of these solutions contained in a hollow glass prism, and it is allowed to solidify while placed between the poles of an electro-magnet, the double refraction persists for several days after the prism is removed from the magnetic field.

M. A. W.

Velocity of Ions produced by a Flame. GIUSEPPE GIANFRANCESCO (*Mem. R. Accad. Lincei*, 1905, [v], 5, 594—619).—The author describes a modification of J. J. Thomson's method for measuring the velocity of ions produced by a flame. Results obtained by the new method show that the variation of the potential in the region between a flame and two plates parallel with it is sensibly the same for the positive as for the negative flame. The curves representing this variation exhibit, however, appreciable differences according as the potential difference between the plates is high or low. The curve has a true maximum corresponding with the top of the flame. The force is zero in the flame, but outside of the latter rapidly increases to a value which is maintained nearly up to the plate, where rapid increase again occurs. Just outside of the flame, the electrical density produced by the ions of either sign reaches a maximum, afterwards falling to a minimum, which is maintained constant over a certain space; near the plate, it increases. The space over which the density remains constant is the smaller the larger the *P.D.* between the plates. The formulæ given by J. J. Thomson and by Child do not accurately express the velocity of the ions. The results obtained are better in accordance with the expression $k = 4\pi i / (X.dX/dx)$, where *i* represents the current and *X* the electric force, and *x* is the direction given by the common

normal to the two plates. All the elements in this formula are measured at one and the same point, so that the velocity obtained is the true specific velocity of the ions at that point and not merely the mean value over a certain space.

The specific velocity of the ions depends on : (1) the intensity of the flame ; (2) the difference of potential between the plates, and (3) the distance from the flame. The numbers obtained agree very well with those given by Mache (*Phys. Zeit.*, 1903, 717), but differ from those of Child (*Phys. Review*, 1899, 12, 65) and of McClelland (*Phil. Mag.*, 1898, 46, 29). The value arrived at for k_n/k_p is in complete accord with that given by Mache (*loc. cit.*) and is very near to that obtained by Zeleny (*Phil. Mag.*, 1898, 46, 133). T. H. P.

Specific Heat of Superheated Steam. LUDWIG HOLBORN and FRITZ HENNING (*Ann. Physik*, 1905, [iv], 18, 739—756).—The authors have determined the specific heat of superheated steam relatively to that of air, and find that the mean value (c_θ) of the specific heat of water vapour between 0° and θ° and at the constant pressure of one atmosphere is given satisfactorily by the formula :

$$c_\theta = 0.4460(1 + 0.000096\theta).$$

The increase of specific heat with temperature involved in this formula is not so rapid as that which has been deduced from explosion experiments. J. C. P.

Fusion, Boiling-point, and Vapour Composition Curves (760 mm. pressure) in the Binary Systems Ortho- + Para-, Ortho- + Meta-, Para- + Meta-bromonitrobenzene; Fusion Curves for Mixtures of Diphenylamine and Phenanthrene. J. VON NARBUTT (*Zeit. physikal. Chem.*, 1905, 53, 697—714).—The boiling-point curves in the case of the isomerides rise continuously from the boiling point of the more volatile constituent to that of the less volatile constituent. As the differences between the boiling points of the pure substances are small, the vapour composition curves in all cases are nearly straight lines. The fusion curves in all cases are of the simplest type, consisting of two branches which meet at a eutectic point. The two curves obtained when (1) *o*- (2) *p*-bromonitrobenzene is added to *m*-bromonitrobenzene are exactly coincident, whilst the two similar pairs of curves obtained when the ortho- and the para-compounds are taken as solvents exhibit a divergence. Hence the author concludes, in view of Jaeger's work on the tribromotoluenes (*Abstr.*, 1905, ii, 304), that the crystallographic symmetry of *o*- and *p*-bromonitrobenzene is close, *m*-bromonitrobenzene belonging to a different category. The author makes a detailed comparison of the actual fusion curves obtained with the "ideal" fusion curves calculated from Le Chatelier's formula (*Abstr.*, 1894, ii, 272). The agreement is generally good. J. C. P.

Modification of Beckmann's Boiling-point Apparatus. ERWIN RUPP (*Zeit. physikal. Chem.*, 1905, 53, 693—696).—In order to permit the determination of the weight of the solvent as well as its volume, the apparatus described by Beckmann (*Abstr.*, 1902, ii, 303 ;

1903, ii, 533) has been slightly modified. Instead of the inner tube being fused into the outer tube, the latter is provided with a ground neck into which the former fits. The various operations necessary for a molecular weight determination by this modified apparatus are described in detail.

J. C. P.

Distillations in High Vacua. ERNST ERDMANN (*Ber.*, 1906, 39, 192—194).—The method described by Wohl and Losanitsch (this vol., ii, 72) has been already used by the author, and also by Valentiner and Schmidt (*Abstr.*, 1905, ii, 704). The author's method consists in using a glass tube containing charcoal from cocoanut shells in conjunction with the apparatus already described (*Abstr.*, 1904, ii, 20). The need for an absolutely air-tight apparatus is insisted on.

J. J. S.

[**Distillations in High Vacua.**] ALFRED WOHL (*Ber.*, 1906, 39, 513—514).—A reply to E. Erdmann (preceding abstract).

C. S.

Heat of Neutralisation of Strong Acids and Bases, as affected by Temperature and Concentration. A. WÖRMANN (*Ann. Physik*, 1905, [iv], 18, 775—795).—The heat of neutralisation (s) has been determined for several strong acids and bases at temperatures between 0° and 32° . The variation of s with temperature (t) over this interval is satisfactorily represented by the formula $s = s_0 - At$, in which s_0 is the heat of neutralisation at 0° , and A is a constant. It will thus be seen that the temperature-coefficient of the heat of neutralisation increases as the temperature rises. The value of s for potassium salts is greater than for the corresponding sodium salts, and the decrease of s with rising temperature is more marked for the sodium salts than for the potassium salts. There is no appreciable difference in the values of s for nitrate and chloride, although the temperature-coefficient is rather greater in the first case. The heat of neutralisation is independent of the concentration in solutions between $N/2$ and $N/10$ strength. In N -solutions, the heat of neutralisation is greater, whilst trustworthy measurements could not be made in solutions of less than $N/10$ strength.

J. C. P.

Constant Temperature Bath for Low Temperatures. A. GIVEN (*J. Amer. Chem. Soc.*, 1905, 27, 1519—1524).—A bath is described which is designed to maintain the water in it at a constant temperature of 15.6° , and is particularly suitable for adjusting the temperature of pyknometers in sp. gr. determinations. The temperature is regulated by the use of a large ice-box immersed in the water and also by means of a Bunsen burner connected with a gas-regulator. The pyknometers are supported on a shelf and kept immersed in the water in the bath. Modifications have been devised for giving a temperature of 20° . For details of the apparatus, the description and diagrams in the original must be consulted.

E. G.

Direct Proportionality between the Freezing Point of a Mineral Water of the Acid Carbonate Class and the Composition of the Water expressed in terms of the Anhydrous Salts and Normal Carbonates. LUCIEN GRAUX (*Compt. rend.*, 1906, 142, 166—167).—The freezing point of a solution containing

1/10 gram-molecule of sodium carbonate per litre is -0.455° , whilst that of the corresponding solution of sodium hydrogen carbonate is -0.389° , or practically the same as that of a solution containing 1/20 gram-molecule of sodium carbonate per litre, namely, -0.356° . It follows therefore that the osmotic pressure of a solution of sodium hydrogen carbonate is determined by sodium carbonate molecules only, the carbonic acid behaving, from the cryoscopic point of view, as if it were entirely free, and the freezing point of a mineral water of the acid carbonate class is proportional to the number expressing the composition of the water in anhydrous salts and normal carbonates.

M. A. W.

Osmotic Pressure of Dilute Aqueous Solutions. PERCIVAL S. BARLOW (*Proc. Camb. Phil. Soc.*, 1905, 13, (iv), 229—240. Compare Abstr., 1905, ii, 507).—Details of experiments on the measurement of the osmotic pressure of dilute solutions are recorded. On account of the impurities absorbed by the outer water from the air and the slight solubility of the material of the pot, the values obtained for the pressure of very dilute solutions are too small. When the first source of error is guarded against, the experimental values approach more closely to the theoretical ones, but still exhibit considerable deviations.

H. M. D.

Organic Solvent and Ionising Media. II. PAUL WALDEN (*Zeit. physikal. Chem.*, 1906, 54, 131—230. Compare Abstr., 1904, ii, 227).—The author has studied the dissociating power of 49 solvents by taking one solute throughout, namely, tetraethylammonium iodide, and determining the equivalent conductivity, Λ , for various dilutions at the temperatures 0° and 25° . The value of Λ_{∞} was obtained by calculation and extrapolation and the degree of dissociation α was calculated for each solution by the usual formula, $\alpha = \Lambda/\Lambda_{\infty}$. In the great majority of cases, Λ increases with the dilution, as in aqueous solutions; the irregular variation of Λ for a few solvents (aldehyde and acetic acid, for example) is attributed to interaction between solvent and solute.

The author's results are in harmony with the Nernst-Thomson rule, and show clearly the close parallelism between the dielectric constant of the solvent and its dissociating power; the greater the dielectric constant of the solvent, the greater, for a given dilution, is the degree of dissociation of the tetraethylammonium iodide. This will be seen from the following table, in which the solvents which behave normally in regard to variation of Λ are arranged according to their dielectric constants, the corresponding data for water being added for the sake of comparison. The degrees of dissociation are recorded for $N/100$, $N/1000$, and $N/2000$ solution; ϵ is the dielectric constant at 20° .

It will be observed that the dissociating power of solvents belonging to the same homologous series diminishes from the first member upwards (for example, methyl alcohol and ethyl alcohol; methyl thiocyanate and ethyl thiocyanate; benzonitrile and phenylacetoneitrile). Certain solvents (for example, acetaldoxime and tetranitromethane), which do not appear in the following table, supply in another way a

Solvent.	ϵ .	Λ_{∞} at 25°.	Percentage dissociation.		
			$v=100$.	$v=1000$.	$v=2000$.
Water	81.7	112	91	98	99
Formamide	84.0	25	93	98	98
Glycollonitrile	67.9	71.5	93	98	99
Succinonitrile	57.3—61.2	35.5 (60°)	90	95	96
Citraconic anhydride ...	39.5	22.5	82	93	94
Nitromethane	38.2—40.4	120	78	92	93
Furfuraldehyde	36.5—39.4	50	about 78	91	93
Lactonitrile	37.7	40	—	89	91
Acetonitrile	35.8—36.4	200	74	90	92
Methyl thiocyanate ...	33.3—35.9	96	77	89	91
Ethylene glycol	34.5	8	78	89	—
Nitrobenzene	33.4—37.4	40	71	88	90
Methyl alcohol.....	32.5—34.8	124	73	88	90
Methyl cyanoacetate ...	28.8	29.5	69	84	87
Propionitrile	26.5—27.2	165	65	84	87
Ethyl thiocyanate	26.5—31.2	84.5	63	83	86
Ethyl cyanoacetate	26.2—26.7	28.2	65	83	87
Benzonitrile	26.0	56.5	61	80	84
Epichlorohydrin	26.0 (?)	66.8	60	81	85
Acetylacetone	25.1—26.0	79	—	83	87
Ethyl alcohol	21.7—27.4	60	54	78	82
Acetone	20.7—21.9	225	50	74	80
Ethylthiocarbimide	19.4—22.0	106	—	66	—
Acetic anhydride	17.9	76	58	79	84
Benzaldehyde	14.5—16.9	42.5	51	73	78
Phenylacetone	15.0—16.7	36	46	74	79
Acetyl bromide.....	16.2	114	47	73	78
Anisaldehyde	15.5	16.5	—	76	81
Acetyl chloride.....	15.5	about 172	46	72	79
Salicylaldehyde	13.9	25	34	55	61
Methyl sulphate	46.5	43	—	91	93
Ethyl sulphate	about 30.0	43	—	84	86
<i>as</i> -Ethyl sulphite	38.6	26.4	—	94	95
<i>s</i> -Ethyl sulphite	16.0	76	—	50	61

confirmation of the Nernst-Thomson rule. These two substances, contrary to expectation, exhibited practically no dissociating power, and were found to have very low dielectric constants, about 3.4 and 2.2 respectively.

According to Dutoit and Aston (Abstr., 1897, ii, 546. Compare also Dutoit and Friderich, Abstr., 1899, ii, 350; Jones and Carroll, Abstr., 1905, ii, 73), conductivity is determined by the association or polymerisation of the solvent molecules, but the author's results are quite opposed to this view, showing as they do (1) that the value of Λ_{∞} has nothing to do with the association factor of the solvent, (2) that solutions of high conductivity are obtained even with non-associated solvents.

There is remarkable variation in the values of Λ_{∞} for the different solvents, but there is no simple relationship between these values and the dielectric constants. It is shown, however, that for the great majority of the solvents the product of Λ_{∞} and the temperature-coefficient of conductivity is approximately a constant, and equal to 1.30 on the average.

Another empirical relationship found to be widely applicable for different solvents is the one expressed by the formula $\epsilon \sqrt[3]{v} = \text{const.}$ In

this expression, ϵ is the dielectric constant of the solvent and v is the dilution at which, in that solvent, the degree of dissociation of the tetraethylammonium iodide has a given value.

With acetonitrile and epichlorohydrin, other solutes were used besides tetraethylammonium iodide, and it was shown that in these two solvents Kohlrausch's law of the independent migration of the ions is valid.

J. C. P.

Solubility of Mercuric Chloride in Ethyl Acetate and Acetone. A. H. W. ATEN (*Zeit. physikal. Chem.*, 1905, 54, 121—123).—To test a theoretical point referred to in a recent paper (Roozeboom and Aten, *Abstr.*, 1905, ii, 803), the author has redetermined part of the solubility curves for mercuric chloride in ethyl acetate and acetone originally studied by Étard (*Abstr.*, 1894, ii, 442). The chief point of interest is the evident formation of a compound of mercuric chloride and acetone. Below 10° , mercuric chloride is at first readily dissolved by acetone, but after a time the compound $\text{HgCl}_2 \cdot \text{C}_2\text{H}_3\text{O}_2$ is deposited from the clear solution. The two separate solubility curves obtained when mercuric chloride and the compound respectively are the solid phases intersect at 13° and 27 molecular per cent. of mercuric chloride. The transition point is far removed from the composition of the compound, and the latter must be largely dissociated in the solution. The solubility curves for mercuric chloride itself in both ethyl acetate and acetone are nearly parallel to the temperature axis. The values obtained for the solubility are for both solvents markedly less than the values recorded by Étard.

J. C. P.

Solid Solutions. FRÉDÉRIC WALLERANT (*Compt. rend.*, 1906, 142, 100—101).—When fused ammonium nitrate containing 20 to 7 per cent. of potassium nitrate is cooled, two kinds of crystals separate simultaneously above 104° : one isomorphous with potassium nitrate and containing 80 per cent. of ammonium nitrate; the other belonging to the tetragonal system and containing 93 per cent. of the ammonium salt; at 104° , the mixture becomes opaque, and monoclinic crystals are gradually formed at the expense of the two first-formed varieties. The inverse phenomenon is observed in the case of mixtures of caesium and ammonium nitrates. On cooling a fused mixture of 2 parts of ammonium and 1 part of caesium nitrate, cubic crystals are first formed, which, on further cooling, pass into rhombohedral crystals isomorphous with caesium nitrate; these are slowly transformed into a conglomerate of two kinds of mixed crystals, one quadratic and isomorphous with that form of ammonium nitrate which is stable at 82 — 125° (compare *Abstr.*, 1904, ii, 31), the other rhombohedral and isomorphous with caesium nitrate.

These two results afford illustrations of the phenomena of diffusion and crystallisation occurring in isomorphous mixtures which, according to van't Hoff, are to be regarded as solid solutions.

M. A. W.

Mixed Crystals of Alkali Nitrates. FRÉDÉRIC WALLERANT (*Compt. rend.*, 1906, 142, 168—169. Compare *Abstr.*, 1904, ii, 31; 1905, ii, 161, 237, 380; and preceding abstract).—Ammonium and rubidium nitrates mix in all proportions to form mixed crystals,

belonging to three crystalline systems: one, rhombohedral and isomorphous with rubidium nitrate; a second, isomorphous with ammonium nitrate; whilst the third is orthorhombic and isomorphous with thallium nitrate, the two crystals having in fact identical physical properties.

At the ordinary temperature, potassium and ammonium nitrates form a discontinuous series of mixed crystals belonging to three different systems, the first being orthorhombic and isomorphous with potassium nitrate, the second monosymmetric and isomorphous with that variety of ammonium nitrate which is stable between 32° and 82° , and the third isomorphous with ammonium nitrate. M. A. W.

Origin of the Conception of Solid Solutions. P. E. LECOQ DE BOISBAUDRAN (*Compt. rend.*, 1906, 142, 195—196. Compare Wallerant, preceding abstracts).—A claim for priority (Abstr., 1892, 398). M. A. W.

A Crystalline Modification Stable in Two Intervals of Temperature. FRÉDÉRIC WALLERANT (*Compt. rend.*, 1906, 142, 217—219).—When the orthorhombic variety of ammonium nitrate which is stable at 32° is cooled, it breaks down at -16° into hemitropic plates which slowly change into quadratic crystals, and not into rhombohedral crystals as stated originally (Abstr., 1904, ii, 31).

This quadratic variety of ammonium nitrate is stable between -16° and -40° and is identical with the quadratic variety which is stable between 82° and 32° . M. A. W.

Influence of the Colouring Matter of the Mother Liquor on the Form of Crystals deposited in it (Phthalic Acid). P. GAUBERT (*Compt. rend.*, 1906, 142, 219—221).—When phthalic acid is crystallised from aqueous solutions coloured with organic dyes, the normal form and size of the crystal are modified, and the crystals absorb a small quantity of the colouring matter, becoming coloured, but not uniformly throughout their mass. The amount of colouring matter absorbed is very small ($1/220$ in the case of bismarck-brown), and has no influence on the density, melting point, or angular values of the crystal. The artificially coloured crystals exhibit pleochroism.

The original contains a description of the dominant forms of the crystals of phthalic acid deposited from solutions containing methylene-blue, magenta, rosaniline, bismarck-brown, biebrich-scarlet, malachite-green, methyl-green, methyl-violet, or diphenylamine-blue. M. A. W.

Laws of the Reciprocal Action of Solid Substances in Cryohydrate Mixtures and in Eutectic Alloys. FLAVIAN M. FLAWITZKY (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 862—875).—The author deduces the following relations between the compositions and solidifying points of cryohydrate or eutectic mixtures and the solidifying points of their components.

1. *Law of Equal Molecular Freezing-point Depressions.*—Assuming that the molecular freezing-point depressions of each of two sub-

stances in the other are equal, as is often the case, it is shown that the ratio between the amounts of the two present in the eutectic mixture is represented by the expression: $n_0 = \sqrt{M_1 T_1} / \sqrt{M_0 T_0}$, where T_0 and T_1 are the differences between the freezing point of the eutectic mixture and those of the two components having the molecular weights M_0 and M_1 , and n_0 the ratio between the percentage contents of the second and first of the two compounds present in the mixture.

2. *Law of Multiple Molecular Depressions.*—When, however, the two substances with molecular weights of M_0 and M_1 occur in the solid form in a polymerised or associated state, the association factors being p and q , the relation becomes $n_0 = \sqrt{q M_1 T_1} / \sqrt{p M_0 T_0}$, from which the association ratio, $p : q$, can be calculated.

3. *Law of the Equivalence of Molecular Freezing-point Depressions.*—This law states that the degree of polymerisation is a characteristic constant for any substance and remains unchanged in binary mixtures.
T. H. P.

Chemical and Electrical Study of the Equilibria $6\text{H}^+ + 5\text{I}^- + \text{IO}_3^- \rightleftharpoons 3\text{I}_2 + 3\text{H}_2\text{O}$ and $6\text{H}^+ + 5\text{Br}^- + \text{BrO}_3^- \rightleftharpoons 3\text{Br}_2 + 3\text{H}_2\text{O}$. VIKTOR SAMMET (*Zeit. physikal. Chem.*, 1905, 53, 641–691).—Full details are given of work already reported (see Luther and Sammet, *Abstr.*, 1905, ii, 508).
J. C. P.

Acceleration of certain Oxidation Reactions by Hydrogen Cyanide. ARTHUR S. LOEVENHART (*Ber.*, 1906, 39, 130–133. Compare Kastle and Loevenhart, *Abstr.*, 1903, ii, 537).—Whilst some catalytic reactions are retarded by hydrogen cyanide, it accelerates the catalytic decomposition of hydrogen peroxide by copper or iron or their salts, and therefore accelerates also oxidations such as that of formic acid or of phenolphthalin by hydrogen peroxide in presence of copper sulphate (compare Weehuizen, *Abstr.*, 1905, ii, 489). This is explained on the assumption that the first stage in the catalytic decomposition, as also in the oxidation, is the formation of an additive compound of hydrogen peroxide and the catalyst. Those substances which decompose hydrogen peroxide catalytically must be capable of existence in two states of oxidation, and the velocity of the oxidation by means of hydrogen peroxide must depend on the ease with which the catalyst changes from one state of oxidation to the other. Whilst cupric sulphate is reduced to cuprous sulphate only by strong reducing agents, the hydrogen cyanide converts it partially into cupric cyanide, which readily changes into the cuprous salt.
G. Y.

Velocity of Electrolytic Reduction of Azobenzene. P. FARUP (*Zeit. physikal. Chem.*, 1906, 54, 231–251. Compare Haber, *Abstr.*, 1900, ii, 257; Haber and Russ, *Abstr.*, 1904, ii, 309).—A silver nitrate voltameter and a cell containing an alkaline solution of azobenzene in aqueous alcohol were placed in series and a suitable current passed. The volume of hydrogen evolved in the cathode compartment of the azobenzene cell was compared with the weight of silver deposited in the voltameter, and the amount of azobenzene reduced could thus be calculated. The azobenzene cell was provided with a rotating cathode,

and the author has studied the manner in which the velocity of reduction is influenced by the rate of revolution of the cathode, by the concentration of the azobenzene, and by the composition of the solvent.

For a given concentration, the velocity of reduction increases as the number of cathode revolutions increases, but gradually approaches an upper limit when the speed of revolution is very great. The velocity of reduction being represented by the formula $dx/dt = k(a-x)^n$, it is found that for moderately concentrated solutions (0.07—0.025 normal) and a low speed of revolution, $n = 1$ nearly; for higher speeds of revolution, n gradually diminishes, and becomes $= 2/3$ when the number of revolutions is 300—1000 per minute, and $= \frac{1}{2}$ when the speed has risen to 5000—6000 per minute. The velocity of reduction is little affected by altering the relative proportions of water and alcohol, but falls off slightly as the concentration of sodium hydroxide increases.

J. C. P.

New Form of Water-pump. ANTOINE VILLIERS (*Ann. Chim. anal.*, 1906, 11, 9).—In this apparatus, the water enters a bulb in which is a small hole fitting immediately above the narrow end of a conical tube. The bulb and tube are surrounded by a wider tube and bulb, the latter being provided with a side-tube through which the air is drawn. The outer tube is constricted to fit the bottom of the inner, conical tube.

W. P. S.

Delivery Funnel for introducing Liquids under Increased or Diminished Pressure. T. J. BRYAN (*J. Amer. Chem. Soc.*, 1906, 28, 80—84).—The apparatus described is a modification of the ordinary stoppered tap-funnel. From the top of the pear-shaped bulb, a side-tube passes downwards and opens into a wide tube surrounding the long delivery tube of the tap-funnel. The upper end of this wide tube is sealed on to the delivery tube; it passes through the cork of the reaction flask, into which it opens a little below the cork. The space above the liquid in the bulb of the tap-funnel is thus brought under the same pressure as that in the flask, and on opening the tap the liquid runs in by its own weight. Modifications of the apparatus are described with the aid of diagrams.

E. G.

A New and Improved Chronograph. ROBERT L. MOND and MEYER WILDERMANN (*Zeit. physikal. Chem.*, 1906, 54, 294—304).—For illustrations and details of construction, the original must be consulted.

J. C. P.

Shaking Machine. ALFRED MANDL and FRANZ RUSS (*Chem. Zeit.*, 1906, 30, 19).—The apparatus consists of a metal box, the temperature of which may be kept constant by means of a thermo-regulator; inside the box is the shaking apparatus proper, for details of which the original paper must be consulted.

P. H.

Inorganic Chemistry.

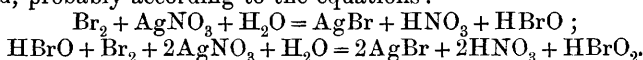
Density of Ice. ANATOLE LEDUC (*Compt. rend.*, 1906, 142, 149—151).—The author has redetermined the sp. gr. of ice by weighing the water which, when frozen, fills a flask of known volume (about 100 c.c.) up to a definite mark. In order to expel completely all the dissolved air, the water, which had been boiled previously, was frozen in a vacuum, melted, and frozen again, and the operation repeated three or four times until on finally freezing the water very gradually under atmospheric pressure, but protected from the atmosphere by a column of liquid vaseline, the ice obtained was quite transparent. The value thus obtained for the sp. gr. of ice at 0° is 0.91752 or, correcting for the contraction of the glass vessel, 0.9176, and differs by about 0.1 per cent. from the value obtained by Bunsen, who used the same method but did not repeat the freezing operation. The author therefore draws the conclusion that water cannot be completely deprived of dissolved air by prolonged boiling; it still contains about 1 c.c. of dissolved gases per litre.

M. A. W.

Action of Strong Hydrochloric Acid on Potassium Chlorate in Presence of Potassium Iodide or Bromide and the Estimation of Chlorate. HUGO DITZ (*Zeit. angew. Chem.*, 1906, 19, 66).—Polemical. A reply to Kolb (this vol., ii, 15).

L. DE K.

Existence of Bromous Acid. A. H. RICHARDS (*J. Soc. Chem. Ind.*, 1906, 25, 4—5).—When liquid bromine is added in large excess to an almost saturated solution of silver nitrate, bromous acid is formed, probably according to the equations:



The presence of bromous acid in the filtered solution was proved as follows: a portion of the solution from which the excess of bromine had been removed by a current of air was first made alkaline with sodium hydroxide and, after the addition of potassium iodide, rendered slightly acid with sulphuric acid. The iodine liberated by the oxygen from the bromous acid was then determined by titration with sodium thiosulphate. A second portion of the original mixture after filtration and extraction with carbon disulphide, to remove free bromine, was reduced with sulphurous acid, the excess of this reagent being subsequently removed by means of potassium permanganate. After making the solution alkaline with sodium hydrogen carbonate, the amount of bromide was determined by titration with *N*/10 silver nitrate. From the above experiments, the ratio of oxygen to bromine was found to agree closely with that required by the formula HBrO_2 .

A further portion of the filtered solution, from which excess of bromine had been removed by a current of air, was made alkaline with sodium hydroxide, treated with excess of sodium bromide, and made acid with sulphuric acid; the bromine thus liberated was estimated by

blowing it into a solution of potassium iodide and titrating the iodine by means of sodium thiosulphate.

The difference between this amount of bromine and the bromine existing in the solution, as shown by the second experiment, gave the amount of bromine liberated from the hydrobromic acid; it was found to be in agreement with the equation $3\text{HBr} + \text{HBrO}_2 = 2\text{Br}_2 + 2\text{H}_2\text{O}$.

These results were confirmed by repeating the last experiment, using the amount of sodium bromide required by the above equation instead of adding, as before, an excess, and finding that at the conclusion of the experiment the solution contained only the faintest traces of bromide.
P. H.

Rapid Preparation of Hydriodic Acid Solutions. F. BODROUX (*Compt. rend.*, 1906, 142, 279—280).—A solution of hydriodic acid is obtained readily by mixing equivalent quantities of iodine and barium peroxide in hot water, adding a second equivalent of iodine to the solution, and passing a stream of sulphur dioxide through the solution until it becomes colourless; the barium sulphate is separated by filtration, and the filtrate, which contains hydriodic acid and a trace of sulphuric acid, is concentrated by distillation. By this method, 140 grams of a solution of hydriodic acid, boiling at 127° and having a sp. gr. 1.67, can be prepared in three hours.
M. A. W.

Chemical and Geological History of the Atmosphere. IV. JOHN STEVENSON (*Phil. Mag.*, 1906, [vi], 11, 226—237. Compare Abstr., 1905, ii, 239).—In a former paper, it was pointed out that the proportion of carbon dioxide in the atmosphere must have varied within wide limits in geological history and that this has been of great importance in bringing about changes in terrestrial climate; in the present paper, the question as to whether the amount of this gas is at present increasing or decreasing is considered. The available analytical data are not sufficient to decide this point, as it is only recently that sufficiently accurate methods have been employed, and local and temporary variations are very difficult to allow for, but it is suggested that something may be learnt by comparison of the proportion of carbon dioxide in inland air with that above the sea, as the latter is a great reservoir of the gas, and owing to its great depth and volume it may be expected to lag behind the atmosphere with respect to variations, and thus exert a regulating effect. From the results of Thorpe and others, the conclusion is drawn that the proportion is smaller in the latter case, so that the amount of carbon dioxide is probably slowly increasing.

Among other factors, the effect of increased coal consumption is discussed. It is considered probable that if the increase continues at the same rate as in recent times, the greater proportion of carbon dioxide arising from this cause will be appreciable in 20 years and in 100 years will be sufficient to bring about modifications in climate. The effect of changes in the amount of this gas on plant evolution is also considered.

It is pointed out that the estimates of the age of the earth arrived

at from physical and geological data are subject to great uncertainty ; in particular, the estimate of Lord Kelvin, deduced from the rate of cooling, may have to be greatly modified when the high absorptive power of carbon dioxide for radiant energy is taken into account.

G. S.

Amorphous Sulphur. III. Nature of Amorphous Sulphur and the Influence of Foreign Substances on the Behaviour of Supercooled Fused Sulphur. ALEXANDER SMITH and WILLIS B. HOLMES (*Zeit. physikal. Chem.*, 1906, **54**, 257—293).—Numerous experiments are described which have contributed to the results already communicated (Abstr., 1903, ii, 139, 284 ; 1905, ii, 382, 580).
J. C. P.

The System Sulphur—Chlorine. A. H. W. ATEN (*Zeit. physikal. Chem.*, 1905, **54**, 55—97. Compare Ruff and Fischer, Abstr., 1903, ii, 204 ; Roozeboom and Aten, Abstr., 1904, ii, 394).—The vapour pressures of mixtures of sulphur chloride and chlorine have been determined at various temperatures, and the character of the variation of vapour pressure with composition shows that at 0° the compound SCl_2 is present in the mixtures and is partly dissociated. The variation of boiling point with composition for mixtures of disulphur dichloride and chlorine confirms the existence of the compound SCl_2 , and indicates also the existence of the compound SCl_4 . It appears further from these boiling-point curves that disulphur dichloride is dissociated to a small extent at its boiling point. It has been possible to determine the boiling point of mixtures containing only the molecules S_2Cl_2 and Cl_2 , for freshly-prepared mixtures of these substances are yellow in colour, whilst mixtures which have stood for some time are red, have a different boiling point, and may be shown to contain at least one compound (SCl_2). It thus appears that the formation of the compound SCl_2 from $\text{S}_2\text{Cl}_2 + \text{Cl}_2$ takes place more or less slowly. Dilatometer experiments, which confirm the existence of the compound SCl_2 , indicate that its formation is a catalytically accelerated reaction, and it is probable that the substance responsible for the acceleration is the compound SCl_4 .

Fusion curves have been determined for mixtures of sulphur chloride and chlorine and of disulphur dichloride and sulphur. The phenomena observed in the former case correspond in the main with those of the ternary system $\text{S}_2\text{Cl}_2 + \text{SCl}_4 + \text{Cl}_2$.
J. C. P.

Conditions of Precipitation and of Solution of Metallic Sulphides. GIUSEPPE BRUNI and MAURICE PADOA (*Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 525—528).—In deriving a general theory of the formation of metallic sulphides and similar precipitates on the basis of the law of mass action and the electrolytic dissociation hypothesis, Ostwald ("Wiss. Grund. anal. Chem.," 1904) stated that the equilibrium $\text{H}_2\text{S} + \text{ZnCl}_2 \rightleftharpoons 2\text{HCl} + \text{ZnS}$ can be displaced towards the right or towards the left, that is, the sulphide will be precipitated or dissolved, according as the concentration of the hydrogen sulphide in the solution is increased or diminished.

To test this statement, the authors have examined the action of hydrogen sulphide under pressures of about 14—16 atmospheres on solutions of certain metallic salts, the reaction of the solution being such that no precipitate would be formed under the ordinary pressure. The hydrogen sulphide was liquefied in the bottom of a stout glass tube immersed in a mixture of solid carbon dioxide and ether in a Dewar's vessel, a small test-tube, with a glass rod fused into the bottom to serve as a foot, and containing the salt solution, being subsequently added. The stout-walled tube was then sealed up in the blowpipe flame and allowed to assume gradually the ordinary temperature of the air, at which the hydrogen sulphide exerts the pressure given above.

Concentrated solutions of ferrous, zinc, and cadmium sulphates and of cobalt and nickel chlorides, all containing acid, yielded abundant precipitates of the corresponding sulphides, but manganous sulphate gave no precipitate under these conditions. After a few days, the sealed tubes were again immersed in the freezing mixture, when it was found that none of the precipitates underwent solution; the zinc sulphide dissolved on heating the liquid. The explanation of the fact that the sulphides do not dissolve when the pressure in the tube is lowered is not clear.

No precipitation is produced by passing hydrogen sulphide through an acid solution of cadmium sulphate if the surrounding space is kept at a low pressure. Also cadmium sulphide, after precipitation in the ordinary way, redissolves completely if a current of air or hydrogen is passed subsequently through the solution.

T. H. P.

Electrolytic Oxidation of Ammonia and its Dependence on the Material of the Anode. ERICH MÜLLER and FRITZ SPITZER (*Zeit. Elektrochem.*, 1905, 11, 917—931).—A solution containing sodium hydroxide and ammonia is used, and the cathode surrounded by a cell of porous earthenware. At a platinum anode, a large quantity of gas is evolved (nitrogen with a little oxygen) and sodium nitrate and traces of nitrite formed in solution. The anodic polarisation of the platinum is greater in presence of ammonia than it is in a solution of sodium hydroxide, probably owing to the formation of nitrate.

With anodes of copper, nickel, iron, and cobalt, the products are nitrogen, oxygen, and sodium nitrite; the proportions in which these are formed depend on the metal used; with cobalt some nitrate is also formed. The anodic potential is in all cases lower than that observed with platinum.

The anodic potential of platinum is much diminished by the addition of salts of copper, nickel, cobalt, or silver to the electrolyte; the products also become similar to those obtained with anodes of the metals in question. The platinum anode becomes coated in these cases with the oxide of the metal added. The same effect is obtained by using a platinum anode previously coated with the oxide of one of the metals mentioned.

A copper anode soon becomes coated with copper oxide, and the oxidation of ammonia to nitrite then takes place almost quantitatively.

T. E.

Production of Nitrites and Nitrates by the Electrolytic Oxidation of Ammonia in the Presence of Cupric Hydroxide.

II. WILHELM TRAUBE and ARTHUR BILTZ (*Ber.*, 1906, 39, 166—178. Compare Abstr., 1904, ii, 727; also Muller and Spitzer, *ibid.*, 1905, ii, 242, and preceding abstract).—The nitrate in all the experiments was estimated by Busch's method (Abstr., 1905, ii, 282). The following are the chief conclusions obtained from numerous experiments. Ammonia can be oxidised electrolytically at the anode provided copper salts and an alkali hydroxide are present. A soluble alkaline earth may be substituted for the fixed alkali. When no free alkali is present, the formation of nitrite ceases, but if care is taken to keep the anode compartment permanently alkaline, the production of nitrite continues until a very concentrated solution is obtained. In addition to the nitrite formation, a small amount of nitrate is also produced at the expense of the nitrite. The amount of this is small at the beginning, but tends to increase, even when an excess of alkali is present, as the ratio concentration of nitrite/concentration of ammonia increases.

The conversion of nitrite into nitrate in the strongly alkaline liquid is accelerated by the presence of small amounts of cupric hydroxide. This has been proved by parallel experiments with solutions, the one containing the copper hydroxide and the other not, but otherwise identical in all respects.

If the amount of alkali hydroxide in the anode compartment becomes less and less and finally completely disappears, so that at the end only an ammoniacal solution is present, it is found that a rapid oxidation of nitrite to nitrate occurs, but even this is accelerated by the presence of the cupric hydroxide so long as free alkali is still present. The amount of copper used in the experiments was small, never more than 0.38 gram per 100 c.c. of solution.

When solutions containing ammonia and cupric hydroxide are electrolysed with platinum or iron electrodes, the formation of a thin black deposit on the anode is observed. This deposit is apparently a peroxide of copper.

J. J. S.

New Hydroxylamine-sulphonic Acids. FRITZ RASCHIG (*Ber.*, 1906, 39, 245—248. Compare Abstr., 1887, 549, 635; Haga, *Trans.*, 1904, 85, 78; *ibid.*, 1906, 87, 240).—*Potassium hydroxylamineisodisulphonate*, $\text{SO}_3\text{K}\cdot\text{NH}\cdot\text{O}\cdot\text{SO}_3\text{K}$, separates in hard crystals from a slowly cooled solution of potassium hydroxylaminetrisulphonate in hot, slightly acidified water. It differs from the ordinary disulphonate in forming anhydrous crystals and in not giving a coloration with lead peroxide in warm water; it is stable at 100° , whereas the trisulphonate, which contains the same percentage of sulphur and potassium, undergoes decomposition at this temperature. The imino-hydrogen atom is replaceable by metals. Excess of boiling dilute hydrochloric acid decomposes the *isodisulphonate* into sulphuric acid and hydroxylamine. The intermediate *isomonosulphonic acid* has not been isolated; it differs from the known hydroxylamine-monosulphonic acid, $\text{OH}\cdot\text{HN}\cdot\text{SO}_3\text{H}$, in possessing oxidising properties, liberating

iodine from potassium iodide, and is therefore regarded as the amide of Caro's acid, $\text{H}_2\text{N}\cdot\text{O}\cdot\text{SO}_3\text{H}$. C. S.

Arsenic Pentafluoride. OTTO RUFF and HUGO GRAF [and, in part, HELLER] (*Ber.*, 1906, 39, 67—71).—Arsenic pentafluoride, prepared by the action of bromine and antimony pentafluoride on arsenic trifluoride, is a colourless gas which condenses at -53° to a clear, pale yellow liquid and solidifies at -80° to a white mass. It dissolves in water and in alkalis with development of heat, and fumes in the air like sulphur trioxide. It does not attack dry glass when cold, but a vigorous action results if a trace of moisture or of hydrogen fluoride is present; silicon has no action when cold, but on heating, arsenic and silicon tetrafluoride are produced. Most metals act on the gas in a similar way, liberating arsenic. The gas has the normal composition and vapour density for the formula AsF_5 . T. M. L.

α - and β -Silicic Acids. FRANZ MYLIUS and ERICH GROSCHUFF (*Ber.*, 1906, 39, 116—125).—A solution A, containing 1 per cent. of silicon dioxide and 0.97 per cent. of sodium chloride, is prepared by mixing the required amount of hydrochloric acid with an aqueous solution of the sodium silicate, $\text{Na}_2\text{Si}_2\text{O}_5$ (Kohlrausch, *Abstr.*, 1893, ii, 166). The α -silicic acid in this solution differs from colloidal or β -silicic acid in that it is not precipitated by egg-albumin at 0 — 18° , by methylene-blue, or by sodium hydroxide. A solution of α -silicic acid may be obtained also by neutralisation of a cooled aqueous solution of silicon chloride with sodium hydroxide. α -Silicic acid changes when heated, or more slowly at the laboratory temperature, into colloidal silicic acid, which is precipitated by egg-albumin, even from solutions containing 0.02 per cent. of silicon dioxide. The conversion of the α - into the β -modification is accelerated by the presence of sodium silicate, and therefore, if the sodium silicate solution is neutralised fractionally, the β -silicic acid only is obtained.

The change from the α - into the β -modification is accompanied by a change in the conductivity of the solution from $k \times 10^6 = 14,032$ for the freshly-prepared solution A to $k \times 10^6 = 14,083$ for a solution seven days old, and by a change in the freezing point from -0.648° for the freshly-prepared solution to -0.608° after three days at 0° , to -0.580° after two days at 18° , and to -0.530° after one and a half hours at 100° . The molecular weight of α -silicic acid is calculated to be about 155; that of colloidal silicic acid has been shown by Sabanéeff (*Abstr.*, 1891, 145) to be not less than 49,000.

If the solution A is cooled to -20° , ice separates and there remains a watery liquid, from which sodium chloride is precipitated on addition of alcohol; when evaporated, the liquid deposits crystals of sodium chloride together with an amorphous mass of hydrated silicon dioxide. If cooled to -25° , the liquid deposits a further quantity of ice and forms a cryohydrate which solidifies; this, when warmed, again becomes liquid without depositing silicon dioxide.

Whilst solutions of alkali silicates of the types R_4SiO_4 , R_2SiO_3 , and $\text{R}_2\text{Si}_2\text{O}_5$, which are strongly hydrolytically dissociated, contain only α -silicic acid, solutions of commercial water-glass contain also

β -silicic acid, as the solutions obtained on neutralisation immediately precipitate egg-albumin. G. Y.

Sodammonium and Potassammonium. ALEXANDRE JOANNIS (*Ann. Chim. Phys.*, 1906, [viii], 7, 5—118).—A detailed account of the work done by the author on sodammonium and potassammonium during the past seventeen years (compare Abstr., 1890, ii, 209, 319, 560, 643; 1891, ii, 642; 1892, ii, 275, 773; 1893, ii, 115, 462, 520; 1894, ii, 280; 1895, ii, 75; 1905, ii, 450); a complete bibliography is appended. M. A. W.

Volatility and Dissociation of Alkali Carbonates. PAUL LEBEAU (*Bull. Soc. chim.*, 1906, [iii], 35, 5—8. Compare Abstr., 1903, ii, 477; 1904, ii, 121; and von Wittorf, Abstr., 1904, ii, 400).—A known weight of the alkali carbonate was placed in a platinum boat and heated in a porcelain tube through which a slow current of carbon dioxide was passed, the tube being heated in an electric furnace. Under these conditions, lithium carbonate proved to be non-volatile when heated at temperatures from 780° to 1200° , and the carbonates of sodium, potassium, and rubidium showed very small and negligible losses in weight. Cæsium carbonate lost 0.32 per cent. of its weight at 1110° .

One gram of cæsium carbonate contained in a platinum boat, placed in a platinum tube, which was rendered vacuous and heated to 720° , gave off 1.5 c.c. of carbon dioxide in thirty-five minutes. The salt dissociates therefore at a temperature much below that at which it begins to volatilise. T. A. H.

Molecular Weight of Silver Vapour. H. VON WARTENBERG (*Ber.*, 1906, 39, 381—385. Compare Nernst, Abstr., 1903, ii, 636).—The vapour density of silver at 2000° was determined by Nernst's method (*loc. cit.*). The statement by that author that silver is not volatile at 1950° was made in error. To protect the iridium bulb from the action of the silver vapour, the inside was coated repeatedly with a solution of zirconium and yttrium nitrates and the bulb heated to a high temperature.

The results are plotted in curves, with the time in seconds as abscissæ, and the displacement n of the mercury thread as ordinates. As the silver tends to condense in the cool, upper portion of the apparatus before the displacement of the mercury has reached the maximum, n observed is too small, and the molecular weight therefore found is too large unless the mercury thread is drawn out almost to the calculated maximum before the silver is added to the bulb.

The molecular weight of silver vapour at 2000° , as determined by this method, was 107 and 111. At this temperature, the molecule of silver vapour is monatomic. G. Y.

Reduction of Silver and of Copper Chloride by Calcium. L. HACKSPILL (*Compt. rend.*, 1906, 142, 89—91. Compare Abstr., 1905, ii, 585).—When an intimate mixture of silver chloride and calcium turnings is heated to dull redness in a vacuum in a porcelain tube,

the chloride is reduced and a silver-calcium alloy formed, the composition of which varies with the proportion of calcium and silver chloride in the original mixture. Homogeneous alloys containing 6.3, 13.3, or 16 per cent. of calcium were obtained in the form of brittle, grey solids having a crystalline fracture, whilst one containing 44.9 per cent. of calcium formed a spongy mass. All the alloys are readily oxidised when heated in the air, and are decomposed by cold water.

A copper-calcium alloy, similarly prepared, contained 18.3 to 18.8 per cent. of calcium and 1.2 to 0.9 per cent. of silicon and formed an orange-yellow, brittle solid, closely resembling the silver-calcium alloys in properties (compare Setlick, *Chem. Zeit.*, 1905, 29, 218).

M. A. W.

Action of Silver Nitrate on Disodium Orthophosphate in Dilute Solution. WILLIAM R. LANG and WILLIAM PEROT KAUFMANN (*J. Amer. Chem. Soc.*, 1905, 27, 1515—1519).—It is usually supposed that solutions of silver nitrate and disodium orthophosphate interact in accordance with the equation: $\text{Na}_2\text{HPO}_4 + 3\text{AgNO}_3 = \text{Ag}_3\text{PO}_4 + 2\text{NaNO}_3 + \text{HNO}_3$. From a study of the reaction under different conditions, it appears that it takes place in several distinct stages, and generally results in the formation of a silver phosphate containing about 76 per cent. of silver (Ag_3PO_4 requires $\text{Ag} = 77.32$ per cent.). It is also found that free nitric acid remains in the solution together with some phosphoric acid, which is not precipitated by the further addition of silver nitrate.

E. G.

Preparation of Metallic Calcium by Electrolysis. SAMUEL A. TUCKER and J. B. WHITNEY (*J. Amer. Chem. Soc.*, 1906, 28, 84—87).—Notes of experiments made with the object of improving the yield in the preparation of calcium by the electrolysis of the fused chloride.

E. G.

Properties of Electrolytic Calcium. L. DOERMER (*Ber.*, 1906, 39, 211—214).—The explosions which take place when electrolytic calcium, either in the form of powder or shavings, is struck on an anvil seem to be due to the presence of oxide of iron (compare Goodwin, *Proc. Amer. Phil. Soc.*, 43, 381). Calcium powder when heated evolves hydrogen, which is reabsorbed on raising the temperature to a low red-heat. When a pile of calcium powder is ignited, it burns throughout at a white heat; occasionally, however, only a feeble combustion takes place, and some unburnt calcium remains. Such calcium has a yellowish colour and is more resistant towards moist air than ordinary calcium; it has a granular, crystalline fracture and is less tenacious.

C. S.

Presence of a Gaseous Hydride of Calcium in Technical Acetylene. CAMILL HOFFMEISTER (*Zeit. anorg. Chem.*, 1906, 48, 137—139).—It was noticed that the acetylene prepared from some specimens of calcium carbide, even after being filtered through cotton-wool and passed through water, gave a deposit of calcium oxide in the conducting pipes, a fact which seemed to indicate the presence of a

volatile calcium compound in the gas. To investigate the matter further, a large volume of the gas obtained from calcium carbide was passed through a number of wash-bottles containing acetone and then through an ammoniacal copper solution to remove the acetylene completely; a colourless, gaseous residue was thus obtained, which burned in the air to calcium oxide and water and formed an exceedingly explosive mixture with oxygen. The gas has not yet been obtained quite free from air, so that its quantitative composition could not be determined.

G. S.

Composition of Bleaching Powder. II. WOLDEMAR VON TIESENHOLT (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 834—862. Compare Abstr., 1902, ii, 562).—In confirmation of the view that bleaching powder consists of a mixture of calcium chloride and hypochlorite, the author finds that: (1) chlorine is evolved from bleaching powder or from a mixture of calcium or lithium hypochlorite with calcium chloride by the action of either moisture or carbon dioxide; (2) when pounded with carbon tetrachloride, bleaching powder is separated into two powders, which differ in their densities and contents of active chlorine. The evolution of chlorine from aqueous solutions of bleaching powder is preceded by the hydrolysis of the calcium hypochlorite with formation of hypochloric acid. The action of carbon dioxide in the evolution of chlorine also depends on the liberation of hypochloric acid and the neutralisation of the lime simultaneously formed. The fact that calcium chloride is the most suitable of the metallic chlorides to bring about the reaction $\text{Ca}(\text{OCl})_2 + \text{CaCl}_2 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{Ca}(\text{OH})_2 + 2\text{Cl}_2$ is ascribed to the peculiar properties of its compounds with water of crystallisation.

T. H. P.

Phosphates of Calcium. I. FRANK K. CAMERON and ATHERTON SEIDELL (*J. Amer. Chem. Soc.*, 1905, **27**, 1503—1512. Compare Abstr., 1905, ii, 33).—The composition has been determined of the solutions and solids in contact with them in the system water, lime, and phosphoric acid under conditions of final equilibrium at 25° and at different concentrations. The concentration of phosphoric acid (P_2O_5) varied up to nearly 540 grams per litre and that of the lime (CaO) to a maximum of 77 grams per litre.

Solutions were made by adding (1) tricalcium phosphate and (2) dicalcium phosphate to phosphoric acid solutions of concentrations up to about 200 grams per litre, and (3) monocalcium phosphate containing an excess of acid to water until a permanent solid residue was obtained. The solid phase in contact with the solution after equilibrium had been reached was identified as dicalcium phosphate, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, in each case.

In two other series of experiments, monocalcium phosphate and dicalcium phosphate respectively were added to solutions of phosphoric acid which were more concentrated than those used in the previous experiments. In each case, the solid phase remaining consisted of monocalcium phosphate, $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$.

The results of the experiments are tabulated, and a chart is given representing the concentrations of the solutions in phosphoric acid (P_2O_5) and lime (CaO). It has been found that with concentrations of

phosphoric acid above 317 grams of P_2O_5 per litre, the stable solid phase at 25° is monocalcium phosphate, and below that concentration down to 20 grams per litre the solid phase is dicalcium phosphate. It is shown that either tricalcium phosphate can exist under equilibrium conditions in contact with water over but a very narrow range of concentration, or that it exists only as a metastable form which changes but slowly into the stable form.

The results of the investigation show that the relative values of mono- and di-calcium phosphates as manures cannot be entirely accounted for by the difference in their solubilities. E. G.

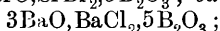
Phosphates of Calcium. II. FRANK K. CAMERON and JAMES M. BELL (*J. Amer. Chem. Soc.*, 1905, 27, 1512—1514).—Experiments have been made with the object of determining the equilibrium conditions for lower concentrations of phosphoric acid and of lime than those used by Cameron and Seidell (compare preceding abstract).

Solutions were prepared by adding lime-water or dicalcium phosphate to solutions of phosphoric acid of concentrations varying from 20 grams to 0.012 gram of P_2O_5 per litre. In the case of solutions prepared by adding dicalcium phosphate to solutions of phosphoric acid of concentrations from 19.96 to 3.66 grams per litre, the solid phase was found to be dicalcium phosphate. In the case of solutions made by the addition of dicalcium phosphate to solutions of phosphoric acid of concentrations from 1.516 grams to 0.381 gram per litre, and by adding lime-water to phosphoric acid solutions containing 0.19—0.015 gram per litre, the ratio $P_2O_5:CaO$ varies from 1.17 to 0.85 and the solid phases over this range are evidently solid solutions. (The ratio for tricalcium phosphate is 0.84.) For very low concentrations of phosphoric acid, there is a quantity of lime in solution and the solid phase is again a solid solution.

The results of the experiments are tabulated and show that the ratio $P_2O_5:CaO$ in the limiting solid solution must be above 1.10 or below 1.27, and that the composition of the liquid solution at that point is between 0.40 and 0.54 gram CaO and between 1.11 and 1.52 grams P_2O_5 per litre. E. G.

Compounds of the Halides and Borates of Strontium or Barium. LÉON OUVARD (*Compt. rend.*, 1906, 142, 281—283. Compare Abstr., 1905, ii, 635; this vol., ii, 86).—The salt, $3SrO.SrCl_2.5B_2O_3$, obtained by fusing a mixture of boron trioxide and strontium chloride with or without the addition of strontia (not more than 1 mol. for each mol. of boron trioxide), forms long needles, showing longitudinal extinction, unaltered by cold water or dilute acetic acid. When the proportion of strontia is increased, the borates, $SrO.B_2O_3$ or $2SrO.B_2O_3$, are formed as large, crystalline plates or prisms respectively; these compounds are, however, readily hydrated by the action of water, and in order to isolate them the fused product is suspended in a tall vessel of water with a layer of glycerol at the bottom; as the mass disintegrates, the crystals fall to the bottom, and are protected by the glycerol from the action of the water. The borate, $SrO.B_2O_3$, forms the hydrate, $SrO.B_2O_3.2H_2O$; and the borate,

$2\text{SrO}, \text{B}_2\text{O}_3$, is decomposed by water forming strontium hydroxide and the crystalline *hydrate*, $\text{SrO}, \text{B}_2\text{O}_3, 4\text{H}_2\text{O}$. When strontium bromide or barium chloride or bromide replace strontium chloride in the above reactions, the following compounds are obtained respectively: *strontium bromoborate*, $3\text{SrO}, \text{SrBr}_2, 5\text{B}_2\text{O}_3$; *barium chloroborate*,



barium bromoborate, $3\text{BaO}, \text{BaBr}_2, 5\text{B}_2\text{O}_3$; and the barium *borates*, $\text{BaO}, \text{B}_2\text{O}_3$ and $2\text{BaO}, \text{B}_2\text{O}_3$, which yield the *hydrates* $\text{BaO}, \text{B}_2\text{O}_3, 2\text{H}_2\text{O}$ and $\text{BaO}, \text{B}_2\text{O}_3, 4\text{H}_2\text{O}$ respectively.

Attempts to prepare strontium or barium iodoborates were unsuccessful.

M. A. W.

Hydrates of Glucinum Sulphate. MARIO LEVI-MALVANO (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 502—510).—Hexahydrated glucinum sulphate crystallises alone only from highly supersaturated solutions, a mixture containing tetrahydrate being mostly obtained on adding hexahydrate to solutions of the tetrahydrate. When once prepared, the hexahydrate does not readily change into the tetrahydrate, but can be obtained by evaporation of even dilute solutions at various temperatures. The cryohydrate of the solution of hexahydrate, which is obtained at about -30° , consists of fine crystals of hexahydrate, a fact which seems to exclude the existence of a hydrate containing more than $6\text{H}_2\text{O}$. The hexahydrate is octahedral in habit and melts at 78.8° . The solubility curve of the hexahydrate cuts that of the dihydrate at about 77.4° , which is hence the transformation temperature at the ordinary pressure.

The tetrahydrate forms octahedral crystals, has the cryohydric point -21° , and is converted into the dihydrate at about 113.6° . Its solubility curve lies roughly parallel with, and close to, that of the hexahydrate.

The solubility curve of the dihydrate is given from 77.4° to about 158° , at which temperature it melts partially and becomes transformed into the monohydrate.

T. H. P.

Sodium-aluminium, Sodium-magnesium, and Sodium-zinc Alloys. C. H. MATHEWSON (*Zeit. anorg. Chem.*, 1906, 48, 191—200).—These alloys were investigated by Tammann's thermal method (see this vol., ii, 10), and the conclusions confirmed by microscopic investigations and in some cases by chemical analysis.

Sodium and aluminium are not mutually soluble and do not form chemical compounds.

Magnesium saturated with sodium contains about 2 per cent. by weight of the latter metal, and the freezing point is lowered from 650° to 638° . On the other hand, sodium dissolves about 1.6 per cent. of magnesium at 657° ; the latter metal separates out completely in hexagonal crystals as the temperature falls, so that the melting point of sodium is not altered.

Sodium and zinc are also only partially miscible, but form a chemical compound already described by Rieth and Beilstein (*Annalen*, 1862, 123, 245; 1863, 126, 248). All mixtures containing from 3.2 up to at least 60 per cent. by weight of sodium show a break in

the cooling curve at 557° . At this point, the temperature of the eutectic crystallisation, there is a non-variant equilibrium, the phases of which are the crystals of the compound, a saturated solution of sodium in zinc, practically pure melted sodium (zinc is almost insoluble in sodium), and the vapours of the two metals. The saturated solution of sodium in zinc contains about 3 per cent. by weight of the former metal. Thermal and direct analyses gave slightly different values for the composition of the compound, the approximate formula of which is NaZn_{11} or NaZn_{12} . It is grey in colour, harder and more brittle than zinc, and only slowly acted on by water. G. S.

Alloys of Thallium with Copper and Aluminium. FR. DOERINCKEL (*Zeit. anorg. Chem.*, 1906, **48**, 185—190).—The cooling curves of these alloys were determined and the conclusions arrived at by Tamman's method of thermal analysis (*Abstr.*, 1904, ii, 113 ; 1905, ii, 444 ; this vol., ii, 10) confirmed by microscopic observations.

Thallium and copper are only partially miscible ; at 959° (the melting point of copper), the layer rich in copper contains 35.1 per cent. by weight of thallium, the layer rich in the latter metal only 1.8 per cent. of copper. The eutectic point of the alloy rich in thallium lies at 302° , 9° below the melting point of thallium. The solubility curves could not be determined by Tamman's method, as the thermal change on admixture is too small. The two metals do not form any chemical compound or mixed crystals.

Thallium and aluminium are not mutually soluble to any appreciable extent ; they do not enter into chemical combination or form mixed crystals. G. S.

Influence of Small Quantities of Elements in Copper on its Reactions with Nitric Acid. JOHN H. STANSBIE (*J. Soc. Chem. Ind.*, 1906, **25**, 45—50).—The author has measured the variation in volume and composition of the evolved gas caused by the introduction of small quantities of other elements into pure copper. The reaction was carried out in a small beaker fitted with a rubber cork through which passed a thermometer and two tubes, *A* and *B* ; *A* was of narrow bore and was attached to a burette from which the acid was delivered into the beaker ; *B* was connected to a graduated tube *C*, the lower end of which was connected by rubber tubing to a movable reservoir, for altering the level of the water in the apparatus ; the burette, beaker, and tube *C* were surrounded by water-jackets. The experiments were carried out as follows : 1 gram of the metal in the form of filings which had been sifted through brass gauze with 64 meshes to the linear inch, and had been treated with a magnet to remove any particles of iron from the file, were placed in the dry beaker ; after filling the jackets around the burette and the beaker with hot water, the acid was allowed to run slowly into the beaker, the temperature being noted. When the reaction was finished, the gas was transferred to the graduated tube *C* by running in water through the burette ; after reading the volume, a measured quantity of oxygen was added to the gas, and, after shaking the tube to remove the last traces of nitrogen peroxide, the volume of residual gas was again read off. In this way, the volume of nitric

oxide originally present in the collected gas could be determined, and this, together with the volume of nitric oxide already removed by the oxygen of the air present in the apparatus at the beginning of the experiment, gave the total volume of nitric oxide liberated from the acid solution. The copper used in these experiments was obtained by fusing the electrically deposited metal under charcoal in a carbon crucible and allowing it to solidify under charcoal so as to prevent the absorption of oxygen during solidification. It was found that an increase in the temperature at which the reaction takes place causes a considerable increase in the volume of nitric oxide liberated and a slight decrease in the volume of gas other than nitric oxide; accordingly, 65° was fixed on as the temperature for carrying out these experiments, the acid used being of sp. gr. 1.2. Alloys of copper with arsenic, antimony, and bismuth were prepared by adding weighed quantities of alloys rich in these metals to pure copper melted under charcoal in a carbon crucible. Owing to the tendency of the bismuth alloys to liquefy and reject bismuth, their composition was not so uniform as those of antimony and arsenic. The results of experiments with ten alloys each of copper with arsenic, antimony, or bismuth are expressed in the form of tables and curves showing in each case the total volume of the gas evolved and the volume of the nitric oxide. It is shown that the presence of impurities in copper even in very small proportions modifies the reaction of the metal with nitric acid, the effect being altogether out of proportion to the quantity of impurity present. In a pure copper arsenic alloy, the arsenic is present as arsenide, and it is the relation of the arsenide to the excess of copper which confers on the alloy its characteristic properties. The condition of most intimate relation of the arsenic with the whole of the copper would be furnished by a perfect solid solution. Thus, the minimum action would be given by the alloy containing the percentage of the added metal which gave the most perfect solid solution. If this view is correct, the point is reached for copper-arsenic when the arsenic equals 0.25 per cent. and for copper-antimony when the antimony equals 0.5 per cent. The behaviour of the copper-bismuth alloys seems to indicate the absence of solid solutions from their compositions. P. H.

Metallic Substitution. ALBERT J. J. VANDEVELDE and C. E. WASTEELS (*Bull. Acad. roy. Belg.*, 1906, 461—512. Compare Abstr., 1903, ii, 200; 1904, ii, 549).—The authors have investigated the action of various substances on the replacement of copper in aqueous solutions of copper sulphate by metallic zinc.

Influence of Non-electrolytes.—Sucrose and alcohol diminish the velocity of substitution, and this effect becomes greater as the concentration of sucrose or alcohol is increased. The retarding influence of sucrose is maintained throughout the reaction. In the case of alcohol, when small quantities are employed, this retarding influence only exists in the initial stages; later on, the rate of substitution is accelerated. The retardation is due to the diminution of the conductivity and diffusibility of the solution as the result of the addition of alcohol or sucrose. The final acceleration by alcohol of the rate of substitution is probably due to the formation and precipitation of

basic zinc sulphate (compare Abstr., 1904, ii, 549, and Ericson-Aurén and Palmaer, Abstr., 1902, ii, 64).

Influence of Neutral Electrolytes.—All the salts used give an initial increase in the velocity of substitution. This increase is not proportional to the concentration of the salt, but reaches a maximum for a certain optimum concentration of the salt (compare Ericson-Aurén and Palmaer, *loc. cit.*). In all cases, the precipitate formed contains at first zinc hydroxide, and towards the end of the reaction some basic zinc sulphate is also deposited (Abstr., 1904, ii, 549).

Influence of Acid Electrolytes.—Sulphuric acid was the only acid electrolyte the action of which was investigated. The phenomena in this case are very complex. At very low concentrations, the acid diminishes the velocity of the reaction, but when the concentration is increased, the velocity of reaction augments and increases with further concentration (compare Kajander, Abstr., 1881, 344). The initial "period of induction" observed by Spring and van Aubel (Abstr., 1887, 1074) in the action of sulphuric acid on zinc appears to be reduced to zero when copper sulphate is present.

Detailed tables showing the results of the experiments made, and illustrating the above conclusions, are given in the original.

T. A. H.

Cuprous Silicide. ÉMILE VIGOUROUX (*Compt. rend.*, 1906, 142, 87—89. Compare *Procès-verb. Soc. Sci. phys. nat. Bordeaux*, 1901).—Cuprous silicide, Cu_4Si , is obtained free from iron when 17 parts of pure silicon and 90 parts of electrolytic copper are fused in a current of hydrogen and the uncombined silicon removed from the product by the action of 5 per cent. sodium carbonate solution. It has a metallic appearance, and a silver-white colour rapidly darkening, becoming first yellow and finally brick-red; it is hard, brittle, and easily powdered, has a sp. gr. 7.48, that of the fused substance being 7.58; it is readily attacked by chlorine, by warm dilute or concentrated nitric acid, or by a mixture of nitric and hydrofluoric acids, whilst hydrochloric, sulphuric, or hydrofluoric acid has hardly any action on the compound (compare Lebeau, this vol., ii, 29).

M. A. W.

Cuprosilicon, and a New Method of preparing Silicon Soluble in Hydrofluoric Acid. PAUL LEBEAU (*Compt. rend.*, 1906, 142, 154—157).—When a mixture of copper and silicon is fused and cooled rapidly, the cuprosilicon obtained after the removal of free silicon by treatment with 10 per cent. sodium carbonate solution contains 12.64 to 12.93 per cent. of silicon, whilst the compound obtained by the gradual cooling of the fused mixture contains 11.31 to 11.36 per cent.; the difference between these values and that required for the compound Cu_4Si , namely, 10.04 per cent. (compare this vol., ii, 29, and Vigouroux, preceding abstract), is due to the presence of uncombined silicon in the form which is soluble in hydrofluoric acid (compare Moissan and Siemens, Abstr., 1904, ii, 560).

The cooling curves for copper and silicon indicate the existence of only one definite compound, Cu_4Si , melting at 800° .

M. A. W.

A New Type of Compound in the Group of Rare Metals. CAMILLE MATIGNON and E. CAZES (*Compt. rend.*, 1906, 142, 83—85).—Anhydrous samarium chloride, SmCl_3 (compare Abstr., 1902, ii, 263, 505; 1905, ii, 391), can be reduced at a high temperature by dry hydrogen, ammonia, or aluminium powder to form *samarium dichloride* (*samarous chloride*), SmCl_2 . This forms a dark brown, crystalline mass having a sp. gr. 3.687 at 22°, insoluble in carbon disulphide, benzene, toluene, chloroform, or pyridine, or even in alcohol, in which the anhydrous chlorides of the rare metals dissolve so readily (compare Abstr., 1901, ii, 602; 1902, ii, 263). It is decomposed by water, liberating hydrogen and forming samarium oxide and samarium oxychloride.

As praseodymium and neodymium chlorides are not similarly reduced by hydrogen or ammonia at high temperatures, this reaction affords a convenient method of separating samarium compounds from mixtures of compounds of these three rare metals. M. A. W.

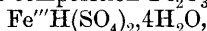
Sulphates of the Rare Metals. CAMILLE MATIGNON (*Compt. rend.*, 1906, 142, 276—278).—The heats of formation of the sulphates of lanthanum, praseodymium, neodymium, and samarium from the acid and generating oxides, calculated from the experimental values for the heats of solution of the oxides in dilute sulphuric acid and the heats of solution of the anhydrous sulphates in water, are 138.2, 125.7, 125.1, and 113.8 Cal. respectively. The basic function of the oxides diminishes from lanthanum to samarium, that is, as the atomic weight of the element increases. M. A. W.

Volatility of Indium Oxide. ALFRED THIEL (*Zeit. anorg. Chem.*, 1906, 48, 201—202. Compare Meyer, this vol., ii, 30).—Polemical. A question of priority. G. S.

Mixed Crystals of Manganese Sulphate and Zinc Sulphate between 0° and 39°. R. SAHMEN (*Zeit. physikal. Chem.*, 1905, 54, 111—120).—The author works out in detail an illustration of Hollmann's theory on the decomposition of hydrated mixed crystals (Abstr., 1902, ii, 446; 1905, ii, 154). Solutions containing manganese and zinc sulphates in various proportions and slightly supersaturated were shaken at several temperatures between 0° and 39°. When sufficient time had elapsed for the attainment of equilibrium, an analysis was made both of the separated crystals and of the solution from which they had separated. The complex results, which do not lend themselves to abstraction, are represented on a diagram indicating the limits of stability of the various types of mixed crystals. The types of mixed crystals involved are: $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ (monoclinic), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (rhombic), $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ (rhombic), $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ (triclinic), $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ (monoclinic). J. C. P.

Effect of certain Elements on the Structure of Cast Iron. ARTHUR H. HIORNS (*J. Soc. Chem. Ind.*, 1906, 25, 50—54).—A detailed account of the influence of varying quantities of silicon, phosphorus, manganese, or sulphur on the formation of crystals of cementite, ferrite, or graphite in cast iron. The paper contains eleven illustrations of sections of the various samples. P. H.

Formation of a New Salt of the Formula $\text{Fe}'''\text{H}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ or $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$. V. KOMAR (*Chem. Zeit.*, 1906, **30**, 15—16).—On evaporating a solution of ferric sulphate in sulphuric acid (containing 400 c.c. of monohydrated acid per litre) to a concentration of 50° B., white crystals, having the composition $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ or

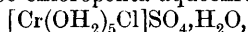


separate; they decompose at 100°, are soluble in water, but are insoluble in sulphuric acid of 45—50° B. P. H.

Nickelo-nickelic Oxide. A Correction. HENRI BAUBIGNY (*Compt. rend.*, 1906, **142**, 154. Compare this vol., ii, 91).—A further reply to Bellucci and Clavari (*Abstr.*, 1905, ii, 824).

M. A. W.

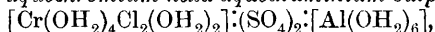
Chromium Salts. ALFRED WERNER and R. HUBER (*Ber.*, 1906, **39**, 329—338. Compare Werner and Gubser, *Abstr.*, 1901, ii, 453; Werner, *Abstr.*, 1902, i, 686; Weinland and Koch, *Abstr.*, 1904, ii, 488).—Recoura's chromium chlorosulphate (*Abstr.*, 1902, ii, 562), which is considered to be chloropenta-aquochromium sulphate,



is formed by dissolving violet chromium sulphate (Higley, *Abstr.*, 1904, ii, 565) in boiling fuming hydrochloric acid; if allowed to crystallise slowly, it forms large, green leaflets. On treatment with barium chloride, it yields a chromium chloride, which crystallises in green needles, behaves towards silver nitrate as an impure dichlorotetra-aquochromium chloride, $[\text{Cr}(\text{OH}_2)_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$, and when treated with sulphuric acid is reconverted into Recoura's chlorosulphate.

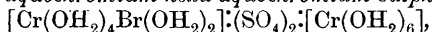
The product obtained on saturating a concentrated aqueous solution of green chromium chlorosulphate with hydrogen chloride, under cooling with ice and salt, is a mixture of dichlorotetra-aquochromium and hexa-aquochromium chlorides. The green chlorosulphate has therefore the constitution $[\text{Cr}(\text{OH}_2)_6] \cdot (\text{SO}_4)_2 \cdot [\text{Cr}(\text{OH}_2)_4\text{Cl}_2] \cdot 2\text{H}_2\text{O}$. In agreement with this, it can be prepared by the action of concentrated sulphuric acid on a mixture of 1 mol. of violet chromium sulphate and 2—6 mols. of green chromium chloride.

Dichlorotetra-aquochromium hexa-aquoaluminium sulphate,



is formed by the action of sulphuric acid on a mixture of aluminium sulphate and green chromium chloride; it is precipitated from its aqueous solution on adding sulphuric acid in small, light green crystals.

Dibromotetra-aquochromium hexa-aquochromium sulphate,



prepared by heating violet chromium sulphate with hydrobromic acid of sp. gr. 1.49, separates from the ice-cooled solution in glistening, dark green crystals or more slowly in large leaflets. G. Y.

Chemistry and Crystallography of the Silicomolybdates. H. COPAUX (*Ann. Chim. Phys.*, 1906, [viii], **7**, 118—144).—Sodium silicomolybdate is readily prepared by heating a mixture of sodium silicate and molybdic acid in the proportion $12\text{MoO}_3 : \text{SiO}_2 : 2\text{Na}_2\text{O}$,

with a little water in a sealed tube at 150° (compare Parmentier, Abstr., 1881, 880; 1882, 702). The free acid can be obtained from the sodium salt by acidifying its dilute aqueous solution and extracting with ether (compare Drechsel, Abstr., 1887, 703, and Asch, Abstr., 1902, ii, 83), or more directly, and with a yield of 75 per cent. of the theoretical, by mixing warm aqueous solutions of ammonium molybdate and sodium silicate in the proportion of $12\text{MoO}_3:\text{SiO}_2$, adding excess of sulphuric acid, and extracting the cooled liquid with ether. Silicomolybdic acid, $\text{SiO}_2, 12\text{MoO}_3, 2\text{H}_2\text{O}, 31\text{H}_2\text{O}$, forms yellow, efflorescent, tetragonal crystals [$a:c=1:1\cdot007$]. The *potassium* salt, $\text{SiO}_2, 12\text{MoO}_3, 2\text{K}_2\text{O}, 18\text{H}_2\text{O}$, is very soluble, 1.076 gram of a solution saturated at 14° containing 0.448 gram of the anhydrous salt; it crystallises in the hexagonal system [$a:c=1:0\cdot6809$]. The acid potassium salt, $2(\text{SiO}_2, 12\text{MoO}_3), 3\text{K}_2\text{O}, \text{H}_2\text{O}, 27\text{H}_2\text{O}$, is monoclinic [$a:b:c=1\cdot200:1:0\cdot860$; $\beta=77^{\circ}39'$].

The *sodium* salt, $\text{SiO}_2, 12\text{MoO}_3, 2\text{Na}_2\text{O}, 14\text{H}_2\text{O}$, forms triclinic crystals [$a:b:c=1\cdot633:1:0\cdot544$; $\alpha=96^{\circ}30'$, $\beta=89^{\circ}23'$, $\gamma=85^{\circ}39'$], whilst the *salt*, $\text{SiO}_2, 12\text{MoO}_3, 2\text{Na}_2\text{O}, 22\text{H}_2\text{O}$, forms triclinic crystals which are too efflorescent to admit of measurement; 1.527 grams of solution saturated at 14° contain 1.056 grams of the anhydrous salt. The *acid sodium* salt, $2(\text{SiO}_2, 12\text{MoO}_3), 3\text{Na}_2\text{O}, \text{H}_2\text{O}, 32\text{H}_2\text{O}$, is monoclinic [$a:b:c=1\cdot341:1:0\cdot999$; $\beta=79^{\circ}32'$].

The *lithium* salt, $\text{SiO}_2, 12\text{MoO}_3, 2\text{Li}_2\text{O}, 29\text{H}_2\text{O}$, forms cubic crystals. The *barium* salt, $\text{SiO}_2, 12\text{MoO}_3, 2\text{BaO}, 29\text{H}_2\text{O}$, forms large octahedra belonging to the cubic system, whilst the *hydrate*, $\text{SiO}_2, 12\text{MoO}_3, 2\text{BaO}, 22\text{H}_2\text{O}$, forms rhombohedral crystals [$a:c=1:2\cdot573$], and the lower *hydrate*, $\text{SiO}_2, 12\text{MoO}_3, 2\text{BaO}, 16\text{H}_2\text{O}$, forms monoclinic crystals [$a:b:c=1\cdot811:1:1\cdot554$; $\beta=75^{\circ}45'$]. The *strontium* salt, $\text{SiO}_2, 12\text{MoO}_3, 2\text{SrO}, 26\text{H}_2\text{O}$,

forms rhombohedral crystals [$a:c=1:2\cdot639$]. The *calcium* salt, $\text{SiO}_2, 12\text{MoO}_3, 2\text{CaO}, 31\text{H}_2\text{O}$, forms cubic octahedra, and the lower *hydrate*, $\text{SiO}_2, 12\text{MoO}_3, 2\text{CaO}, 26\text{H}_2\text{O}$, is isomorphous with the corresponding strontium salt. *Salts* of the type $\text{SiO}_2, 12\text{MoO}_3, 2\text{MO}, 31\text{H}_2\text{O}$, where M = Mg, Zn, Mn, Ni, or Co, crystallise in octahedra belonging to the cubic system and have characteristic colours, those of zinc and magnesium being yellow, manganese orange, copper and nickel green or greenish-blue, and cobalt garnet-red. The *cadmium* salt, $\text{SiO}_2, 12\text{MoO}_3, 2\text{CdO}, 22\text{H}_2\text{O}$,

forms triclinic crystals [$a:b:c=0\cdot440:1:0\cdot383$; $\alpha=88^{\circ}43'$, $\beta=91^{\circ}14'$, $\gamma=84^{\circ}42'$]; the *silicomolybdates* of *iron*, *aluminium*, and *chromium* have the general formula, $3(\text{SiO}_2, 12\text{MoO}_3), 2\text{M}_2\text{O}_3, 93\text{H}_2\text{O}$, and are isomorphous with the magnesium series of salts.

The silicomolybdates are usually isomorphous with the corresponding silicotungstates, which they also closely resemble in degree of hydration and solubility: the mercurous, thallium, rubidium, and ammonium salts of the two series being very sparingly soluble, whilst the alkaloid silicomolybdates are as insoluble as the corresponding silicotungstates.

The potassium salts of silicomolybdic and of silicotungstic acid containing $18\text{H}_2\text{O}$ form hexagonal crystals closely resembling those of quartz, and they are dextrorotatory, whilst their solutions are optically

inactive; laevorotatory crystals of these salts can also be obtained from solutions containing traces of alkali impurity; dextro-potassium silicomolybdate crystals have $[\alpha]_D +17.0-17.4^\circ$ and the laevo-crystals $[\alpha]_D -17.1^\circ$.

M. A. W.

Electrolytic Preparation of Spongy Tin. DONATO TOMMASI (*Compt. rend.*, 1906, 142, 86).—Spongy tin can be prepared by electrolysing a solution consisting of 50 parts of water, 10 parts of stannous chloride, and 1 part of hydrochloric acid, using two tin anodes situated on either side of a revolving cathode formed of a copper disc, and so arranged that part only is immersed in the liquid, the exposed part revolving between two mechanical brass scrapers, which remove the spongy tin and depolarise the cathode. The spongy tin is collected, drained, and washed, the washings concentrated to the strength of the original solution, and returned to the bath. With a cathode of 3 cm. diameter and a current of 40 amperes and 3 volts, the yield of spongy tin per hour is 86.36 per cent. of the theoretical quantity.

M. A. W.

Auto-oxidation of Tervalent Titanium. WILHELM MANCHOT and P. RICHTER (*Ber.*, 1906, 39, 320—323).—When titanium sesquioxide is shaken with aqueous potassium hydroxide and oxygen, it is found that a considerably larger volume of oxygen is absorbed than corresponds with one equivalent of oxygen. The hydrogen peroxide primarily formed is reduced partially by the titanium sesquioxide, the remainder of the peroxide oxidising the titanium dioxide to pertitanic acid on acidification or possibly even in the alkaline solution. If a thick milk of lime or baryta water is used in place of the potassium hydroxide, the hydrogen peroxide formed is not reduced by the titanium sesquioxide or dioxide, and the whole of the oxygen absorbed is found in the form of hydrogen peroxide. If the solution of trivalent titanium in sulphuric acid is boiled with potassium hydroxide, it evolves a volume of hydrogen equal to that of the oxygen absorbed on shaking the alkaline solution with oxygen. The acid solution also evolves hydrogen when boiled, but only extremely slowly. When shaken with oxygen, a solution of trivalent titanium in sulphuric acid containing ferrous ammonium sulphate absorbs a still larger excess of the gas, and the solution contains ferric oxide, whereas an acid solution of ferrous ammonium sulphate alone does not absorb a measurable volume of oxygen.

G. Y.

Oxidation of Tervalent Titanium. II. WILHELM MANCHOT and P. RICHTER (*Ber.*, 1906, 39, 488—492. Compare preceding abstract).—When titanium sesquioxide is added to a solution of chromic and hydriodic acids dissolved in the requisite amount of water, the liberated iodine may be estimated by thiosulphate. For the oxidation, 3 atoms of oxygen were required for 1 atom of titanium. The oxidation of titanium sesquioxide with permanganic acid in the presence of tartaric acid also led to a similar result.

A. McK.

Preparation of Titanium Tetrachloride and of Tin Tetrachloride. CARL RENZ (*Ber.*, 1906, 39, 249—250).—When the vapour of chloroform is passed over finely-divided titanium oxide heated in a hard glass tube, the main reaction proceeds according to the equation: $\text{TiO}_2 + 2\text{CHCl}_3 = \text{TiCl}_4 + 2\text{CO} + 2\text{HCl}$. The temperature determines the nature of the by-products, among which carbon dioxide, phosgene, and hexachlorobenzene have been identified, together with a colourless gas, probably titanium hydride, TiH_4 . In a prolonged reaction, reduction of the titanium oxide and titanium tetrachloride takes place with the formation of titanium, titanium dichloride, and titanium trichloride.

Tin tetrachloride, but not silicon tetrachloride, may be obtained in a similar way. C. S.

Thorium-aluminium Alloy. OTTO HÖNIGSCHMID (*Compt. rend.*, 1906, 142, 280—281).—The compound ThAl_3 , prepared by the direct union of aluminium and thorium in a vacuum at a high temperature or by reducing potassium thorium fluoride or thorium oxide with aluminium in the electric furnace, forms long, prismatic needles having the colour and metallic aspect of aluminium. It burns in fluorine or chlorine, is attacked by bromine or iodine without incandescence, is stable in the air, but burns when heated to redness. It is attacked by the mineral acids, is unaltered by alkali solutions, but oxidised with incandescence by the fused alkali hydroxides or carbonates.

M. A. W.

A Silicide of Thorium. OTTO HÖNIGSCHMID (*Compt. rend.*, 1906, 142, 157—159).—*Thorium silicide*, ThSi_2 , is prepared by the interaction of a mixture of the double fluoride of thorium and potassium, potassium silicofluoride, and aluminium at 1200°, and purified from free aluminium and silicon by treatment with potassium carbonate solution. It forms quadratic plates resembling graphite in colour, has a sp. gr. 7.96 at 16°, and when heated combines readily with the halogens, oxygen, sulphur, selenium, or hydrogen chloride, but is not attacked by hydrogen at a red heat. It is soluble in aqueous solutions of the mineral acids, is not attacked by solutions of the alkalis, but is decomposed on fusion with sodium or potassium hydroxides. For analysis, the compound was dissolved in aqua regia or in a mixture of hydrofluoric and nitric acids, or decomposed by fusing with moist sodium hydroxide. Thorium silicide can also be prepared by heating a mixture of thorium oxide and silicon in an electric furnace with a current of 700 amperes and 100 volts, or by heating a mixture of aluminium, silicon, and thorium at 1000°.

M. A. W.

Mixtures of Antimony and Tellurium and of Antimony and Selenium. Cryoscopic Constant of Antimony. HENRI PÉLABON (*Compt. rend.*, 1906, 142, 207—210).—When mixtures of antimony and tellurium are fused, the telluride Sb_2Te_3 is formed, which yields a homogeneous liquid with excess of either constituent, and the cooling curve exhibits one maximum at the solidification temperature of the

compound, Sb_2Te_3 , and two minima, one corresponding with the point of solidification of the mixture $5\text{Sb} : 2\text{Te}$, and the other with the eutectic point of the mixture, $\text{Sb} : 10\text{Te}$.

Antimony selenide forms homogeneous liquids when fused with excess of either antimony or selenium, but there is a discontinuity in the cooling curve of the mixtures in which the value of R (the ratio of the mass of selenium to the total mass) lies between 11 and 39; such mixtures have two solidifying points at 566° and 518° respectively, the cooling curve consisting of two straight lines parallel to the abscissa along which R is measured. The melting point, 605° , of the compound Sb_2Se_3 is a maximum point and the melting point of the mixture $2\text{Sb} : 7\text{Se}$ is a point of inflexion on the cooling curve.

The cryoscopic constant of antimony, calculated from the depression of its freezing point caused by the addition of antimony telluride, selenide, or sulphide (compare Abstr., 1904, ii, 267), is 1246, 1233, or 1228 respectively.
M. A. W.

Antimony Sulphate and its Double Salts with Alkali Sulphates. SIGMUND METZL (*Zeit. anorg. Chem.*, 1906, 48, 140—155). —When antimony oxide is dissolved in concentrated sulphuric acid and the solution cooled, the normal sulphate, $\text{Sb}_2(\text{SO}_4)_3$, separates in long, glistening needles, which can be freed from adherent acid by drying on porous plates and finally by washing with xylene. The salt has the sp. gr. 3.624 and is very hygroscopic. With cold water it gives the basic sulphate, $\text{Sb}_2\text{O}_3 \cdot \text{SO}_3$ or $(\text{SbO})_2\text{SO}_4$; with excess of hot water it forms a much more basic salt, but cannot be changed completely into the oxide. With alcohol in the cold, the basic salt, $\text{Sb}_2\text{O}_3 \cdot 2\text{SO}_3$, is produced. The contradictory statements regarding this salt in the literature are due to the fact that adherent sulphuric acid cannot be completely removed by drying on porous plates.

Double sulphates of antimony with potassium, sodium, and ammonium have been prepared by heating antimony oxide and the alkali sulphate with concentrated sulphuric acid and then cooling the clear solution. They have the general formula $\text{Sb}_2(\text{SO}_4)_3 \cdot \text{M}_2\text{SO}_4$, occur in long, glistening needles, and are decomposed by water and alcohol with formation of the same basic salts as in the case of the sulphate itself (compare Gutmann, Abstr., 1899, ii, 33). Metallic antimony and the sulphide are only slowly, and in the latter case incompletely, decomposed by concentrated sulphuric acid, but in presence of an alkali sulphate the action goes smoothly and completely; this fact is of importance for the technical preparation of antimony compounds.
G. S.

Peroxides of Bismuth. I. ALEXANDER GUTBIER and R. BÜNZ (*Zeit. anorg. Chem.*, 1906, 48, 162—184. Compare Pattison Muir, *Trans.*, 1881, 39, 22; 1887, 51, 77; Deichler, Abstr., 1899, ii, 428). —The peroxides were prepared by the usual method: the freshly-precipitated hydroxide was suspended in hot concentrated potassium

hydroxide solution and chlorine gas passed in for some time; the precipitate was then washed and treated with concentrated nitric acid to separate the lower from the higher oxides, the latter remaining undissolved. The results are greatly influenced by the nature and strength of the alkali used; the most highly oxidised products were obtained with a large excess of concentrated potassium hydroxide solution of sp. gr. 1.4. It was found impossible to obtain a product of uniform composition and no definite chemical compound could be isolated.

The scarlet powder obtained by the action of concentrated nitric acid of sp. gr. 1.4 on the most highly oxidised precipitates, and regarded by Muir (*loc. cit.*) and others as "bismuthic acid," HBiO_3 , always contains considerably less oxygen than corresponds with this formula and is not a uniform substance; this is in agreement with Deichler's results. On continued washing with the object of freeing it from potassium nitrate, it decomposes with evolution of oxygen and formation of an orange-yellow powder, formerly regarded as hydrated bismuth tetroxide, $\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. Attempts to prepare the latter substance by Deichler's method (*loc. cit.*) were unsuccessful, as no compound of uniform composition could be obtained. The contention of Muir, that "bismuthic acid" changes to the pentoxide at 120° and to the tetroxide at a higher temperature, is inaccurate, since the scarlet powder begins to lose oxygen at 100° .

Neither the scarlet nor the orange-yellow product shows any sign of salt formation on treatment with concentrated potassium hydroxide solution.

G. S.

Boiling of Osmium, Ruthenium, Platinum, Palladium, Iridium, and Rhodium. HENRI MOISSAN (*Compt. rend.*, 1906, 142, 189—195. Compare this vol., ii, 92).—The author has examined the behaviour of the metals of the platinum group at the temperature of the electric arc; the metals were placed in a carbon crucible inside an electric furnace (Abstr., 1893, ii, 167, 314) through which passed a copper tube cooled by a current of cold water. With a current of 500 to 700 amperes and 110 volts, all the metals rapidly fused and entered into ebullition. The metallic distillates consisted of spherules together with microscopic crystals or crystalline plates; the residual ingots showed a crystalline structure in the cases of osmium, platinum, iridium, and rhodium; they all contained graphite: 3.89—3.97 per cent. in osmium; 4.8 per cent. in ruthenium; 2.8 per cent. in iridium, and 2.19 per cent. in rhodium; and palladium exhibited the phenomenon of spitting. Palladium is more readily fusible than platinum, and osmium is the most difficult to distil, the weight of distillate obtained from 150 grams of the metal when heated for five minutes with a current of 700 amperes and 110 volts being 29 grams, whilst the same weight of the other metals heated for the same length of time with a current of 500 amperes and 110 volts gave the following distillates: ruthenium, 10 grams; platinum, 12 grams; palladium, 9.6 grams; iridium, 9 grams; and rhodium, 10.2 grams.

M. A. W.

Oxides of Palladium. Lothar WöHLER and JAMES KÖNIG (*Zeit. anorg. Chem.*, 1906, **48**, 203—204).—Polemical. Reply to Bellucci (this vol., ii, 35). G. S.

Nitrilobromo-osmonates. ALFRED WERNER and KARL DINKLAGE (*Ber.*, 1906, **39**, 499—503).—*Potassium nitrilotetrabromo-osmonate*, $[\text{OsNBr}_4]\text{K}, 2\text{H}_2\text{O}$, prepared from potassium osmiamate and hydrobromic acid of sp. gr. 1.49, forms dark red, monoclinic prisms; its aqueous solution is cherry-coloured.

Ammonium nitrilopentabromo-osmonate, $[\text{OsNBr}_5](\text{NH}_4)_2, \text{H}_2\text{O}$, prepared by the addition of ammonium bromide to the mother liquors resulting from the preparation of the preceding salt, forms dark brown, monoclinic prisms with a reddish-violet tint.

Rubidium nitrilopentabromo-osmonate, $[\text{OsNBr}_5]\text{Rb}_2$, prepared in an analogous manner, forms a dark brown powder with a reddish-violet tint; its aqueous solution is red.

Hydrogen caesium nitrilopentabromo-osmonate, $[\text{OsNBr}_5]_2\text{Cs}_3\text{H}$, is an amorphous, brown powder with a green tint; it is the least soluble in water of the salts described, and its aqueous solution is bright red.

A. McK.

Mineralogical Chemistry.

Kleinite, a Hexagonal Mercury Oxychloride from Texas.
ARTHUR SACHS (*Sitzungsber. K. Akad. Wiss. Berlin*, 1905, 1091—1094).
—This is probably identical with the undetermined yellow mercury oxychloride mentioned by Moses (Abstr., 1904, ii, 46); the small crystals are, however, not orthorhombic, but hexagonal. There is a perfect cleavage parallel to the basal plane, and less distinct cleavages parallel to the faces of a prism. The purest crystals are sulphur-yellow, and have an adamantine lustre, but in the slightly altered crystals the colour is orange-yellow and the lustre is rather duller. The hardness is 3—4; sp. gr. 7.441. Analyses gave: Hg, 86.68—87.13; Cl, 7.63—8.25 per cent., corresponding with the formula $\text{Hg}_4\text{Cl}_2\text{O}_3$. The other mercury oxychlorides recently described by Moses from this locality, Terlingua in Texas, are eglestonite (cubic, $\text{Hg}_6\text{Cl}_3\text{O}_2$) and terlinguaite (monoclinic, Hg_2ClO). L. J. S.

Chemical Study of Sea Waters. THÉOPHILE SCHLOESING (*Compt. rend.*, 1906, 142, 320—324).—Analyses of the water of the Atlantic Ocean and of the Mediterranean show that the two waters differ only in degree of salinity, the composition of the mineral constituents being almost identical in the two cases; the analytical results are given in the following table; 1 litre of water at 20° contains:

	Mediterranean.	Atlantic.	Ratio.
Calcium carbonate	0.127 gram	0.099	0.78
Sulphuric acid	2.551 "	2.120	0.831
Chlorine.....	21.376 "	17.830	0.834
Bromine.....	0.072 "	0.060	0.833
Lime (not included above)	0.599 "	0.519	0.866
Magnesia	2.361 "	1.993	0.844
Sodium oxide.....	16.017 "	13.410	0.837
Potassium oxide	0.510 "	0.413	0.810
	<hr/> 43.613 "	<hr/> 36.444	
Oxygen equivalent of chlorine and bromine	4.824 "	4.024	
Total salts per litre	<hr/> 38.789 "	<hr/> 32.420	0.836

M. A. W.

Formation of Oceanic Salt Deposits. XLV. Formation of Tincal and Octahedral Borax. JACOBUS H. VAN'T HOFF and WALTER C. BLASDALE (*Sitzungsber. K. Akad. Wiss. Berlin*, 1905, 1086—1090).—Potassium borate does not separate from a solution containing this salt and sodium chloride, but only potassium chloride and sodium borate. The saturations of solutions containing sodium borate and sodium chloride in the presence of potassium chloride, sodium sulphate, and glaserite are given for temperatures of 25° and 83°. Below 35.5°, sodium borate separates as tincal ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), but above this temperature it separates as "octahedral" [that is, rhombohedral] borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$). The latter has been observed as a natural product in the lagoons of Tuscany. L. J. S.

Analysis of the Ash which fell in Naples on the Night of October 2nd, 1904. EZIO COMANDUCCI and L. PESCIPELLI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1905, [iii], 11, 249—253).—The Vesuvian ash which fell in Naples at intervals during the night of October 2nd, 1904, is a heavy, granular, dark chocolate-coloured, magnetic powder, having the following percentage composition: SiO_2 , 41.738; SO_3 , 1.518; Cl, 0.242; P_2O_5 , 1.428; Fe_2O_3 , 25.338; Al_2O_3 , 7.714; MgO , 0.214; CaO , 5.310; K_2O , 0.102; Na_2O , 1.917; NH_3 , traces; loss on ignition, 3.72. T. H. P.

Isomorphism and Thermal Properties of the Felspars. ARTHUR L. DAY and EUGENE T. ALLEN (*Zeit. physikal. Chem.*, 1905, 54, 1—54).—The authors have prepared a series of artificial felspars, namely, albite (Ab), anorthite (An), and the following combinations of these: Ab_1An_5 , Ab_1An_2 , Ab_1An_1 , Ab_2An_1 , Ab_3An_1 , Ab_4An_1 . All these, with the exception of albite, were obtained in completely or partially crystalline form by crystallisation from the corresponding fused mass. With the help of a thermoelectric junction, the temperature of fusion was determined for the members of the foregoing series. As the albite end of the series was approached, however, the determination of the melting point became increasingly difficult, owing to the very gradual transi-

tion from the solid to the liquid condition. The melting points obtained were as follows :

An.	Ab ₁ An ₅ .	Ab ₁ An ₂ .	Ab ₁ An ₁ .	Ab ₂ An ₁ .	Ab ₃ An ₁ .
1532°	1500°	1463°	1419°	1367°	1340°

The melting-point curve is continuous, and the view adopted is that the triclinic feldspars are solid solutions, and together form an isomorphous series. It is noteworthy that the solid phase obtained in each case has the same composition as the liquid phase of glass from which it separates. The view that the feldspars form an isomorphous series is strongly supported by a study of the way in which the specific gravity (s_c) of the crystals varies with the composition. This is shown in the following table, which shows also the specific gravity (s_g) of the corresponding glasses :

	An.	Ab ₁ An ₅ .	Ab ₁ An ₂ .	Ab ₁ An ₁ .	Ab ₂ An ₁ .	Ab ₃ An ₁ .	Ab.
s_c	2·764	2·734	2·710	2·680	2·660	2·649	2·6
s_g	2·700	2·648	2·590	2·533	2·486	2·458	2·382

The paper contains many detailed observations on the processes of fusion and crystallisation in these glasses. Thus, amongst other things, it was shown that microscopic crystals of a homogeneous compound might, if slowly heated, retain their form for 200° above the point at which fusion began.

J. C. P.

Physiological Chemistry.

Oxygen Tension in Submaxillary Glands and other Tissues.

JOSEPH L. BARCROFT (*Bio-chem. J.*, 1906, 1, 1—10).—The experiments recorded confirm those of Pflüger and of Külz, who showed that the oxygen tension in the saliva is greater than that in blood-plasma, and that there is a definite oxygen tension in other secretions. Injection of thionin shows that the submaxillary gland does not reduce the dye sufficiently to prevent it from becoming blue throughout. The saliva and urine are also blue. The gland becomes bluer, the muscles less blue, on activity.

In view of the great consumption of oxygen in the submaxillary gland, the high oxygen tension in saliva is not easy to account for, but the most probable explanation is that the capillary walls have the power of raising the tension of the gas as it passes through them.

W. D. H.

Survival Respiration of Muscle. GEORGE T. KEMP and E. R. HAYHURST (*Proc. Amer. Physiol. Soc.*, 1905, xxviii—xxix; *Amer. J. Physiol.*, 15).—Isolated muscle at rest produces carbon dioxide, especially immediately after excision. In frog's muscle there are further increases at the third and sixth hours; then the yield becomes constant

until there is a sudden increase, when putrefaction sets in. In mammalian muscle there is regular, steady fall. Work increases the output, whether the muscle is directly or indirectly stimulated. Temperatures between 18° and 30°, or variations in the speed of the air current bathing the muscles have no effect. If no oxygen is supplied, however, the yield of carbon dioxide is reduced. Curare has no influence on the output from unstimulated frogs' muscles; if the nerves of such muscles are stimulated, the results are inconstant. Curarised mammalian muscle on nerve stimulation gives off more carbon dioxide than when at rest, but this statement at present rests on only three experiments.

W. D. H.

Estimation of the Volume of Blood in Animals. C. GORDON DOUGLAS (*J. Physiol.*, 1906, 33, 493—505).—The volume of the blood estimated in animals by Haldane and Lorrain Smith's carbon monoxide method during life closely corresponds with that found by Welcker's older method after death.

W. D. H.

Ion-proteid Compounds. I. Influence of Electrolytes on the Heart's Frequency. T. BRAILSFORD ROBERTSON (*Pflüger's Archiv*, 1905, 110, 610—624).—Experiments on the frog's heart lead to the conclusion that the frequency of the beat is determined by ions in the fluid which bathes it, and a mathematical formula is given to show what the rate will be if the relative velocities of anions and cations are known. The alternate formation of proteid compounds containing anion and cation is suggested.

W. D. H.

Vagus Inhibition and Salts of the Blood. WILLIAM H. HOWELL (*Amer. J. Physiol.*, 1906, 15, 280—294).—In a circulating fluid containing only the chlorides of sodium, potassium, and calcium, an increase in the potassium salt augments the sensitiveness of the heart to vagus inhibition until it at last itself causes inhibition. Complete lack of potassium is accompanied by a lessening or loss of vagus control. A solution of pure sodium chloride (0.7 per cent.) causes loss of vagus control. An increase of calcium salt has no effect on vagus inhibition of the auricles, but is followed by diminution and finally loss of vagus action on the ventricle (of the terrapin), owing probably to the development of an independent ventricular rhythm. The experiments indicate that inhibition of the heart depends on the presence of diffusible potassium compounds in the heart tissue, and that vagus impulses act indirectly by increasing the amount of potassium compounds of this character.

W. D. H.

Centrifugalisation of Arbacia Eggs. ELIAS P. LYON (*Proc. Amer. Physiol. Soc.*, 1905, xxi—xxii; *Amer. J. Physiol.*, 15).—Centrifugalising unfertilised eggs effects a separation of the egg material into four layers. These are capable of subsequent fertilisation, and develop into plutei normal in all respects except pigmentation. During centrifugalisation, the pigment of the egg collects in the lowest layer. In the pluteus larva it is distributed in every possible way.

W. D. H.

Effect of Alkalis and Acids and of Alkaline and Acid Salts on Growth and Cell Division in the Fertilised Eggs of *Echinus esculentus*. BENJAMIN MOORE, HERBERT E. ROAF, and EDWARD WHITLEY (*Proc. Roy. Soc.*, 1906, 77B, 102—136).—In malignant disease, the secretion of acid by the stomach is reduced owing to a change in the distribution of the salts of the blood which increases its alkalinity. In *Echinus* eggs, small amounts of alkali or alkaline salts stimulate growth and cell division, but the cells are irregular in size and shape, and the cells become multinucleated. An increase of alkali stops the process. Where stimulation occurs, non-typical mitosis like that seen in cancer cells is noticeable. Acid produces no such results; the effect of acid is simply inhibitory. The cells are most sensitive to even slight changes in the concentration of hydrogen and hydroxyl ions.

W. D. H.

Effect of Acid and Alkali and certain Indicators in Arresting or otherwise Influencing the Development of the Eggs of *Pleuronectes platessa* and *Echinus esculentus*. EDWARD WHITLEY (*Proc. Roy. Soc.*, 1906, 77B, 137—149).—The amount of variation from the normal concentration of hydrogen and hydroxyl ions in sea-water which the eggs of *Pleuronectes* will tolerate is very small, a disturbance towards the acid side being more fatal than the opposite. As the eggs grow they become more resistant. Phenolphthalein is deadly to *Echinus* eggs, but harmless to those of *Pleuronectes*. Dimethylaminoazobenzene quickly kills the latter, but influences the former favourably.

W. D. H.

Influence of Chloroform on the Growth of Young Animals. A. SCHAPIRO (*Proc. Physiol. Soc.*, 1905, xxxi—xxxiii; *J. Physiol.*, 33).—Daily anaesthetisation with chloroform retards the growth of young kittens; this is compensated by accelerated growth subsequently.

W. D. H.

Physical Conditions of Colloids. V. The Electrical Charge of Proteids. WOLFGANG PAULI (*Beitr. chem. Physiol. Path.*, 1906, 7, 531—547).—The experiments were made with serum freed as far as possible from electrolytes by dialysis, or with the proteids separated from serum. Such serum shows no appreciable electrical conductivity. If acid is added, the proteid assumes an electro-positive character and is carried to the cathode; if alkali is added, the reverse occurs; sodium chloride and other neutral salts have no effect (compare Hardy, this vol., i, 121); acid or alkaline salts produce the same effect as acids and alkalis. Some conclusions are drawn from this as to the precipitation of proteids by various reagents, and the question is mooted whether changes in the electrical charge of proteids in the body may explain certain physiological phenomena in connection with proteid chemistry and assimilation, immunity, and histological reactions.

W. D. H.

Mechanism of the Pylorus. WALTER B. CANNON. **Movements of Stomach and Intestines.** WALTER B. CANNON and F. T. MURPHY (*Proc. Amer. Physiol. Soc.*, 1905, xxv, xxv—xxvi; *Amer. J. Physiol.*, 15).—The theory that free acid in the stomach is the signal for the

opening of the pylorus is confirmed by observations through a gastric fistula.

After intestinal section and suture, the pylorus remains closed against the peristaltic pressure of the stomach, and food does not enter the injured gut until the intestinal wound is cemented. In intestinal obstruction, violent peristalsis occurs repeatedly in attempts to force the contents against the obstacle. It is then moved backwards to the stomach. Anaesthesia or exposure of the intestines to the air has little or no effect, but handling, even gently, inhibits movements for hours. The actual movements were studied as in previous work by observation with X-rays, the food being mixed with bismuth subnitrate.

W. D. H.

Trypsinogen and Enterokinase. J. MOLYNEUX HAMILL (*J. Physiol.*, 1906, 33, 476—478).—Trypsinogen and enterokinase are not specific for each animal, but are always the same definite chemical individuals although they occur in widely separated classes of the animal kingdom. Enterokinase from any animal is able to activate the trypsinogen of any animal, so far as has yet been investigated.

W. D. H.

Absorption of Proteids from the Intestine. E. PROVAN CATHCART and JOHN B. LEATHES (*J. Physiol.*, 1906, 33, 462—475).—No evidence of any absorption could be obtained in loops of intestine prepared with oxygenated defibrinated blood. The muscular movements continue, but the epithelium of the mucous membrane desquamates. By examining the blood of an animal at intervals during absorption of proteid cleavage products introduced into the intestine, a small increase accounting for about 15 per cent. of the nitrogen absorbed was found in the amount of nitrogenous material in the blood which is not precipitable by tannic acid; a similar increase occurs in the liver. A flow of urine set up during the operation contains a considerable amount of nitrogen. No increase in the coagulable proteids of the blood was detected. The tendency of the experiments is not in favour of proteid synthesis by the intestinal epithelium, although this is not absolutely excluded.

The amount of amino-acid and similar substances found at any moment in the blood should not be taken as an index of the amount of nitrogen absorbed in this form, any more than Kühne was right in arguing from the amount of amino-acid in the intestine that the amount formed there is small; if formed, they are formed for absorption, not for accumulation in the intestine. So with amino-acids in the blood, they are not absorbed for storage in the blood, but are removed from the blood by the tissue cells and dealt with there, being either assimilated with protoplasm or changed and at last discharged as waste material by the kidneys.

W. D. H.

Enzymes of the Embryonic Alimentary Canal. LAFAYETTE B. MENDEL (*Proc. Amer. Physiol. Soc.*, 1905, xiii—xiv; *Amer. J. Physiol.*, 15).—The intestines of embryo pigs were examined for inverting ferments. Maltase is universally present, lactase is present very early,

whilst sucrase is absent. They do not occur in other organs, such as liver and kidney. In adult animals, sucrase is always present, but no lactase. In the sucking-pig, all three are present. There are similar differences in the dog. Lactase was not found in the hen or chick, but sucrase was present in both. Pepsin and rennin are absent from the embryonic stomach of the pig.

W. D. H.

Protective Mechanism of Intestinal Worms. J. MOLYNEUX HAMILL (*J. Physiol.*, 1906, 33, 479—492).—Intestinal parasites resist digestion because they contain an anti-ferment. Dastre and Stassano consider this is anti-kinasic; this would confirm Delezenne's view that enterokinase is not a ferment which acts on trypsinogen, but that trypsin plays the part of an amboceptor to allow enterokinase to attack the proteid molecule. The present experiments were made with an extract of intestinal worms added to solutions of enterokinase, or of trypsin, or of mixtures of the two. They prove that the anti-substance is antitryptic, not antikinasic.

W. D. H.

Metabolism of the Nervous System. WALDEMAR KOCH (*Proc. Amer. Physiol. Soc.*, 1905, xv—xvi; *Amer. J. Physiol.*, 15).—A hypothesis is advanced that in nervous metabolism compounds resembling polypeptides are elaborated from proteid. Such compounds contain 4 per cent. of sulphur in a form which is easily split off as sulphate, and is not present as cystine sulphur. A change in the state of oxidation of the sulphur gives a clue to the rôle played by oxygen in this metabolism. An excess of easily available oxygen is necessary for the vitality of nervous structures, but the yield of carbon dioxide is very low.

W. D. H.

Influence of Normal Salts on the Staining and Fixation of Nervous Tissues. EMIL MAYR (*Beitr. chem. Physiol. Path.*, 1906, 7, 548—574).—The longitudinal fibres of the spinal cord are rapidly swollen and disintegrated by the action of physiological salt solution or by a corresponding solution of sodium sulphate. Distilled water has a similar effect, and even Ringer's solution is not harmless. This occurs most readily in the posterior columns, where, after twenty-four hours' exposure to the salt solution, a neuroglia network is all that remains intact. The fibres of the spinal nerve roots are not affected. This is not due to putrefaction, nor markedly to autolysis, although the experiments do not entirely exclude ferment action. In regard to temperature, there is close correspondence at certain critical temperatures between the action of the salt solution and the coagulation temperatures of the different nerve-proteids, as described by Halliburton. The influence of alcohol and various fixatives on this phenomenon is discussed, as also is their varying effect on the staining reactions of the Nissl granules in the light of our knowledge on the actions of ions.

W. D. H.

Distribution of Chlorides in Nerve Cells and Fibres. ARCHIBALD B. MACALLUM and MISS M. L. MENTEN (*Proc. Roy. Soc.*, 1906, 77B, 165—192).—It has been shown previously that the well-

known reduction staining with silver nitrate so much used in histology is due to the presence of chlorides. The transverse striæ produced at the nodes of Ranvier in nerve-fibres, and known as the lines of Frommann, can be obtained at any portion of the axis cylinder provided means are taken to allow the reagent to get at it. These lines do not indicate, however, a pre-existent distribution of the chlorides in alternating layers. The same appearance can be reproduced in capillary tubes containing egg-white or gelatin impregnated with potassium dichromate (Boehm, Liesegang). Ostwald explains this by supposing that when the critical concentration in the advancing solution is reached, precipitation begins and continues until a stria is formed. This brings the solution back to the metastable condition, then another development of the labile condition obtains, and thus a new stria after an interstria zone is formed. As the silver salt becomes more and more dilute, critical concentration is attained later and later, and so new striæ are separated by interstria zones of increasing width.

The cytoplasm of the nerve cell shows the same appearances, but less intensely; this may be due to difficulty of penetration, but it is held that probably the cell-body is poorer in chlorides than the axon. The nucleus is destitute of chlorides.

The mixture of electrolytes and colloids in the nerve-fibre would not permit the ions carrying the electrical charge to travel unimpeded, and the change of potential transmitted would travel with diminished velocity. This would bring into line the nerve impulse and the action current of nerve. It is freely admitted that caution must be exercised at present in drawing physiological conclusions from physical data, but the following facts are very suggestive: (1) the presence of electrolytes (chloride or chlorides) in a concentrated degree, and uniform in distribution; (2) the maintenance of this concentration through the impermeability of the sheaths of the fibres, and (3) the high conductivity of the axon and the occurrence of electrical phenomena when it is injured.

W. D. H.

Chemistry of Nerve Degeneration. WALDEMAR KOCH and WILLIAM H. GOODSON (*Amer. J. Physiol.*, 1906, 15, 272—279).—The grey matter of the prefrontal and motor areas differs very little in composition. The *corpus callosum*, a mass of white matter, contains less water, less proteid, and more cerebrins. The sciatic nerve contains more connective tissue and more nucleo-proteid. The substance spoken of as the sulphur compound is more abundant in nerve and white matter than in grey matter.

In the degenerated tissues of general paralytics, the water is more abundant, the nucleo-proteids are increased, but the proportion between the other constituents (lecithin, kephalin, cerebrin, &c.) is but little altered, although their absolute amounts are much reduced. In Wallerian degeneration experimentally produced in a dog's spinal cord, the same condition was found. The paper is illustrated by tables of analyses.

W. D. H.

Phrenosine and Cerebrone. HANS THIERFELDER (*Zeit. physiol. Chem.*, 1905, 46, 518—522).—Posner and Gies (this vol., ii, 54)

consider that Thudichum's phrenosine is identical with Thierfelder's cerebrone, and that the latter name ought to be dropped. The identity of the two substances is here disputed. Thudichum's material appears to have been an impure product, and so the name cerebrone should be retained.

W. D. H.

Composition of Nasal Mucous Membrane. BERT RUSSELL and WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1905, xxiii—xxiv; *Amer. J. Physiol.*, 15).—The nasal mucous membrane of the ox contains from 20 to 23 per cent. of solids, about 1 per cent. being ash. Enzymes are absent. The organic material is mainly collagen and proteid including nucleo-proteid. No mucoid is found. The relation between composition and secretion has yet to be studied.

W. D. H.

Oxidation in Tissues in the Presence of Ferric Salts. FR. BATTELLI and Mlle. L. STERN (*Compt. rend.*, 1906, 142, 175—177).—In extracts of muscle, on the addition of a ferric salt, lactic acid is oxidised vigorously with the formation of carbon dioxide. This is considered to be due to the combined action of the iron salt and hydrogen peroxide. In the body, the iron salt is represented by anticalase. The same is true for extracts of other tissues. It is assumed that in the tissues a substance is present termed "peroxydogen," which liberates hydrogen peroxide in the presence of oxygen. This substance disappears soon after death, is destroyed by acid, and preserved by alkali. In the body, nitrogen is not completely burnt, but the chief end-product is urea; the method employed does not oxidise urea, and so a further analogy is drawn between oxidation so produced and that which occurs in the body.

W. D. H.

The Suprarenal Capsules in Cases of Nervous and other Diseases. By FREDERICK W. MOTT and WILLIAM D. HALLIBURTON (*Proc. Physiol. Soc.*, 1906, iii—iv; *J. Physiol.*, 34).—At the autopsies performed on cases which died in the London County Asylums it was frequently noticed that the suprarenal capsules were atrophied or disintegrated. Knowing the close relationship between the nervous system and the suprarenal medulla, from the embryological point of view, it did not appear on *a priori* grounds impossible that there might be a similar connection between nervous disease and suprarenal atrophy. The suprarenals in over seventy successive cases were examined; a small portion of each was reserved for microscopic study; Vulpian's colour reaction with ferric chloride was applied to another portion, and the intensity of the result noted. The remainder was rapidly dried in a vacuum, and extracts of the dried powder were examined physiologically for adrenaline.

The glands were atrophied, degenerated, or disintegrated in about half of the specimens, and in these adrenaline was either absent or present only in traces. But no connection could be traced between such a condition and the original nervous or mental disease for which the patient had been admitted to the asylum. Suprarenal atrophy appears, however, to be related to the secondary diseases from which

the patient ultimately died. In the majority of cases where it occurred, the patients had suffered from chronic diseases. Such diseases, as is well known, affect injuriously the secreting mechanism of the whole body, and the suprarenal apparently shares in this depression. Acute diseases, on the other hand, do not appear to produce these effects so markedly unless they are very intense. The observations suggest the possibility that the fatal termination of chronic diseases may be accelerated by the lack of suprarenal secretion, and consequent circulatory depression.

W. D. H.

Coagulation of the Swimming Plate and Contractility.

RALPH S. LILLIE (*Proc. Amer. Physiol. Soc.*, 1905, xii; *Amer. J. Physiol.*, 15).—The swimming plate of *Eucharis lobata* beats normally 3 to 6 times per second. In a solution of alkaline sodium chloride it becomes much faster, and the colloids become opaque and coagulate, movement ceasing within half a minute. This is explained by the hypothesis that partial coagulation accompanies the normal beat, and repair during the relaxation. If the rate increases, the time for recovery is lessened, and so the colloids progressively coagulate.

W. D. H.

The Chromogen of so-called Scatole-red. LOUIS C. MAILLARD (*Zeit. physiol. Chem.*, 1905, 46, 515—517. Compare Abstr., 1905, ii, 271).—Polemical. The author reaffirms the views stated previously.

W. D. H.

Galvanotropism of Volvox. OLIVER P. TERRY (*Amer. J. Physiol.*, 1906, 15, 235—243).—The galvanotropism of *Volvox* depends on its state of chlorophyll metabolism; normally *Volvox* goes to the cathode. If kept in the dark for two or three days, it goes to the anode. This is reversed on exposure to light. Blue light has little or no effect. Red light stimulates assimilation and affects the organisms like sunlight.

W. D. H.

Gain and Loss of Fixed Alkali in the Body; Estimation of Organic Acids in Urine, with Reference to Diabetes. EDWARD S. EDIE and EDWARD WHITLEY (*Bio-chem. J.*, 1906, 1, 11—27).—Methods are described for estimating in the urine the output of fixed alkali, fixed acid, and organic acid from the body. The total output of organic acid is important in diabetes. Administration of alkali decreases the amount of ammonia, but increases that of organic acids. Just as in acid poisoning the body protects itself by ammonia-formation from urea, so in alkali poisoning there is a similar protection in the increased amount of organic acid formed from carbohydrate.

W. D. H.

Equilibrium in Solutions of Phosphates. LAWRENCE J. HENDERSON (*Amer. J. Physiol.*, 1906, 15, 257—271).—The acidity of urine which can be estimated by titration varies with the temperature, partly because of variations in the ionisation of water. Neglect of this factor may produce an error of 5 per cent. The hydrogen ionisation of serum corresponds to that of solutions in which the ratio of Na_2HPO_4

and NaH_2PO_4 varies between 6 : 4 and 1 : 0. Within this range, variation is harmless to protoplasm ; this is a protective mechanism whereby large amounts of acid or alkali may be immediately neutralised and the hydrogen ionisation preserved within normal limits. The reaction $\text{Na}_2\text{HPO}_4 + \text{H}_2\text{CO}_3 = \text{NaH}_2\text{PO}_4 + \text{NaHCO}_3$ is a balanced one, and even in solutions less acid than monosodium phosphate, sodium hydrogen carbonate cannot exist. Both the determinations of hydrogen ionisation in urine and in phosphate solutions and their behaviour to methyl-orange indicate that urine contains a mixture of mono- and di-hydrogen phosphates.

W. D. H.

Organic Phosphorus in Urine. DOUGLAS SYMMERS (*J. Path. Bact.*, 1905, 10, 427—430. Compare Abstr., 1905, ii, 102).—An increase in excretion of organic phosphorus occurred intermittently in a case of typhoid fever. In a case of extensive organic disease of the central nervous system, the organic phosphorus excretion rose and fell intermittently but the output was not markedly increased. The data are admittedly too few yet for definite conclusions to be drawn.

W. D. H.

Salt Glycosuria. FRANK P. UNDERHILL and OLIVER E. CLOSSON (*Proc. Amer. Physiol. Soc.*, 1905, xx—xxi ; *Amer. J. Physiol.*, 15).—When sodium chloride is injected intravenously in rabbits, polyuria and glycosuria occur, probably as a result of increased permeability of the kidney. This may be decreased by adding calcium chloride. The blood contains less sugar than normal in the former, and more in the latter case. This points to a glycosuria of renal origin. Injection of sodium chloride into the cerebral circulation, or of magnesium sulphate into the ear vein, produces glycosuria but no polyuria. In these cases, the dyspnœa produced explains the condition.

W. D. H.

Excretion of Creatinine in Man. C. J. C. VAN HOOGENHUYZE and H. VERPLOEGH (*Zeit. physiol. Chem.*, 1905, 46, 415—471).—A more detailed account of experiments previously published (this vol., ii, 40), showing that muscular work on ordinary diet leaves the creatinine excretion unaltered (see Folin, Abstr., 1905, ii, 183, 268).

W. D. H.

Treatment of Diabetes by Extract of Duodenum. BENJAMIN MOORE, EDWARD S. EDIE, and JOHN H. ABRAM (*Bio-chem. J.*, 1906, 1, 28—38).—A neutralised acid extract of duodenum given by the mouth alleviates the diabetic condition in young patients. The extract is believed to stimulate the pancreas to form the internal secretion which normally regulates carbohydrate metabolism. At present, the number of cases is too small for positive conclusions to be drawn.

W. D. H.

Pancreatic Diabetes. OSKAR MINKOWSKI (*Pflüger's Archiv*, 1906, 111, 13—60). EDUARD PFLÜGER (*Ibid.*, 61—93).—A distinctly polemical discussion on questions raised by Pflüger's recent work and criticisms. The points principally at issue are whether partial extirpation of the

pancreas will produce a diabetic condition, whether the explanation of the diabetes is a nervous disturbance or due to interference with the internal secretion of the pancreas, and whether the sugar originates from proteid or from fat.

W. D. H.

The Toxin of Dysentery. H. LÜDKE (*J. Path. Bact.*, 1905, 10, 328—333).—A method of obtaining the toxin from the bacilli of dysentery is described. Some of the results brought forward differ from those of previous observers.

W. D. H.

Lactase and Sugar Excretion in Infants with Gastric Diseases. LEO LANGSTEIN and FRANZ STEINITZ (*Beitr. chem. Physiol. Path.*, 1906, 7, 575—589).—In suckling infants with severe gastric disturbance, only a part of the lactose given is resolved by lactase into dextrose and galactose. These products are either burnt in the body, or in the case of galactose, especially if oxidative processes are not efficient, excreted in the urine. A second part of the lactose administered is absorbed as such, and leads to lactosuria. The remaining and largest portion is never absorbed at all, but undergoes fermentative changes in the intestine.

W. D. H.

The Changes in Blood-forming Organs in Typhus Fever. ANDREW LOVE (*J. Path. Bact.*, 1905, 10, 405—417).—In this disease, the bone marrow is the seat of a well-marked neutrophile reaction, and the chief seat of formation of polymorpho-nuclear neutrophile corpuscles. The spleen acts as a scavenger, and its main function is phagocytosis. The lymphatic glands are normal.

W. D. H.

Physical and Chemical Properties of Solutions of Chloroform and other Anæsthetics. **Chemistry of Anæsthesia.** II. BENJAMIN MOORE and HERBERT E. ROAF (*Proc. Roy. Soc.*, 1906, 77 B, 86—102. Compare Abstr., 1904, ii, 501).—Confirmation is given to the theory that chloroform and other anæsthetics form unstable compounds with proteids and produce their effects by thus interfering with the chemical activities of protoplasm. The solubility of the anæsthetics is greater in serum than in water; beyond a certain concentration, which is definite for each anæsthetic, precipitation of the compound with proteid occurs. The vapour pressure is always higher in an aqueous solution than in solutions which contain proteid. Determinations of freezing points and electrical conductivity support the main contention of the paper. When the lipoids extracted from serum or tissues by ether are made into an emulsion with normal saline solution, many of them take the form of bi-concave discs. Such emulsions are very permanent, but separate on the addition of anæsthetics or neutral salts in similar fashion to colloidal solutions.

W. D. H.

Physiological Properties of West African Boxwood. R. J. HARVEY GIBSON (*Bio-chem. J.*, 1906, 1, 39—53).—An alkaloid is present in West Indian boxwood which is shown to be a cardiac poison by experiments on the excised cat's heart; the effect is cumulative. In workmen employing this wood, the poison is evidently dissolved by the moisture on their perspiring hands, and is absorbed, leading to serious cardiac symptoms.

W. D. H.

***p*-Ethoxyphenylcamphorylimide (Camphenal) as an Antipyretic.** ELIJAH M. HOUGHTON (*Proc. Amer. Physiol. Soc.*, 1905, xxvi—xxvii; *Amer. J. Physiol.*, 15).—This substance differs from acetylphenetidine in that an acetyl is replaced by a camphoryl group. In animals, it has no action as an antipyretic. W. D. H.

Hordenine, its Degree of Toxicity, Symptoms of Intoxication. LUCIEN CAMUS (*Compt. rend.*, 1906, 142, 110—113).—Hordenine sulphate is only slightly toxic. It causes death by arresting respiration. Recovery from large doses is very rapid and the weight of the animal is not appreciably affected during the days following recovery. N. H. J. M.

Toxicity of Strychnine, Morphine, and Quinine to Paramœcium. ORVILLE H. BROWN (*Proc. Amer. Physiol. Soc.*, 1905, xxiv; *Amer. J. Physiol.*, 15).—Various salts of the alkaloids named of *m*/100 concentration kill paramœcia in times varying from a few seconds to two minutes. W. D. H.

Pharmacology of a Colloidal Compound of Strychnine. ORVILLE H. BROWN (*Proc. Amer. Physiol. Soc.*, 1905, xxii—xxiii; *Amer. J. Physiol.*, 15).—Fresh egg-albumin, hydrogen peroxide, and a solution of a strychnine salt when mixed form a gel in the course of a few days, which no longer gives the strychnine tests, but when injected into frogs it produces typical strychnine tetanus, which starts about five hours after the injection instead of in a few minutes. W. D. H.

Antitoxic Action of Anions. RALPH S. LILLIE (*Proc. Amer. Physiol. Soc.*, 1905, xiii; *Amer. J. Physiol.*, 15).—The destructive action of the chlorides of calcium, barium, and strontium on the ciliated cells of the mussel is due to the preponderant action of the cation, and is retarded by salts with strongly acting anions. On the other hand, toxicity due to a preponderance of the anion (as in sodium salts) is counteracted by cations. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Production of Methane in Biological Processes. V. OMELIAN-SKY (*Centr. Bakt. Par.*, 1906, ii, 15, 673—687).—Methane is produced by fermentation from cellulose, gum arabic, acetic acid, egg-albumin, glue, gelatin, wool, peptone, and very many other substances. It is probable that all soils containing organic matter yield methane. Hence it is impossible to draw any conclusions as to the nature of the decomposing organic matter from the fact that methane is one of the products.

N. H. J. M.

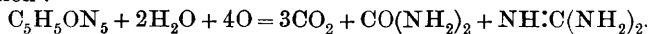
Action of Living Microbes on a Solution of Azure-blue in Methyl Alcohol. F. MARINO (*Ann. Inst. Pasteur*, 1905, 19, 816—820).—The preparation of a staining solution for microbes, similar to Leishman's, is described. To an aqueous solution of methylene-blue a little sodium carbonate is added and the mixture kept at 60—80° until it takes a purple tint, an aqueous solution of eosin is then added, the mixture left for some time, the precipitate collected, and dissolved in methyl alcohol. The best results are obtained when two parts by weight of the blue and one of eosin are employed. Reasons are given for supposing that the blue dye and the eosin are not in stable chemical combination in methyl-alcoholic solution.

When a little of the staining solution is poured into a tube containing a culture of certain bacilli in bouillon in such a way that it forms a layer above the latter, a rose-coloured layer, surmounted by a blue layer, soon forms on the surface of the culture; this effect is due to the reduction of the blue dye by the bacilli, so that the rose colour of the eosin alone appears. Experiments with anthrax and other bacilli show that the rapidity with which the effect described is produced does not depend on the virulence of the different bacilli towards animals; it is the more rapid the greater the number of bacilli, and is favoured by increase of temperature up to 35°. It is suggested that this method might be employed for the detection of microbes which cannot be observed microscopically, but the results so far obtained are not conclusive. G. S.

Bacteriological Examination of some Samples of Abnormal Milk. ROBERT BURRI and M. DÜGGELI (*Centr. Bakt. Par.*, 1906, ii, 15, 709—722).—Four samples of milk were examined: (1) had an odour of Limburger cheese; (2) an odour of dogs; (3) had a bitter taste; and (4) a taste and odour of Glarner Schabzieger cheese. The appearance and characters of the organisms which produced the peculiarities referred to are described. In the case of the milk having an odour of dogs, it was found that whilst the organism produced the odour in peptone broth and some other solutions, it did not have this effect on other samples of milk. It is probable, therefore, that the original sample of milk (2) was abnormal from the commencement.

The organisms responsible for the changes in samples (1) and (3) are very similar, and morphologically identical, or nearly so. The microbe of sample (4) is very much like Escherich's *Bacterium lactis aërogenes*. N. H. J. M.

Fermentation of Guanine. CELSO ULPIANI and MANSANIELLO CINGOLANI (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 596—600).—The authors have isolated from the excrements of pigeons a micro-organism which grows readily in a solution containing a small proportion of inorganic salts together with guanine, which is decomposed yielding urea, guanidine, and carbon dioxide according to the equation:



The organism belongs to the class of coccus-bacteria, forming mostly rods which are about 2 μ in length, with swollen and refractile

extremities, and are distinctly capsuled. It also presents itself in the form of stout filaments 6—8 μ in length and comprising three or four distinct segments furnished with a single capsule. As the culture increases in age, these large filaments become more abundant and the phenomena of bacteriolysis are observed. The organism is stained by Gram's method, by magenta (Ziehl's reagent), which exhibits clearly the capsule, and by gentian-violet, assuming a uniform colouring. It is very motile, the short rods being endowed with a very rapid movement and the larger filaments with a moderately rapid zig-zag motion. The characteristics of the cultures on solid and liquid media are described.

T. H. P.

Oligonitrophilous and Mesonitrophilous Bacteria in the Soil of the Roman Campagna. R. PEROTTI (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 623—629).—From the soil about Rome, the author has isolated two species of *Azotobacter*, probably *A. chroococcum* and *A. agilis*, *Clostridium Pasteurianum*, and certain pseudomonads.

T. H. P.

The Wax of Tubercle Bacilli in Relation to their Acid Resistance. W. T. RITCHIE (*J. Path. Bact.*, 1905, 10, 334—340).—Fatty or waxy substance can be demonstrated by osmic acid, scharlach roth, and Sudan III in tubercle bacilli, in two acid-proof bacilli, and in certain bacteria, such as *Bacillus anthracis*, which are not acid-proof. More occurs in the tubercle bacillus than in bacteria which are not acid-proof. The power of resisting acid, but not alcohol, was restored to a bacillus formerly acid-proof by cultivating it in a fatty medium. The acid resistance is due to a substance soluble in ether. Tubercle bacilli are no longer acid-proof after treatment with boiling xylene, toluene, and other reagents.

W. D. H.

Bacillus Typhosus Simulans. J. G. McNAUGHT (*J. Path. Bact.*, 1905, 10, 380—382).—Two typhoid-like organisms are described as occurring in water not obviously polluted. Distinctions are described in the mode of growth on media.

W. D. H.

Autodigestion of some Yeast Species (Top Fermentation Yeasts, Distillery and Film Yeasts). M. SCHENK (*Chem. Centr.*, 1905, ii, 1812—1813; from *Zeit. Spiritusind.*, 28, 397—399, 409—410, 416. Compare Abstr., 1905, ii, 547).—Top fermentation yeast gives rise to the following products on autodigestion: succinic acid, tyrosine, leucine, adenine, hypoxanthine in traces, glutamic and aspartic acids, arginine, guanidine, lysine, and tetramethylenediamine. Distillery and film yeasts yield, besides most of these substances, lactic acid, uracil, and choline, and somewhat more hypoxanthine, but only traces of glutamic acid. Arginine and guanidine are absent, either because the arginine previously present has been converted into tetramethylenediamine or owing to the action of arginase. The products from top fermentation and distillery yeasts give a marked tryptophan reaction: the film yeast, however, shows no such reaction.

E. F. A.

Importance of Vegetable Organisms for the Oxygen Supply of Water. W. CRONHEIM (*Bied. Centr.*, 1906, 35, 1-5; from *Plöner Forschungsber.*, 1904, 276).—Attention is drawn to the importance of vegetable organisms in supplying the oxygen required by fishes and for the purification of rivers. Schimanski showed that water which in strong light contained 1.8 c.c. of oxygen per 100 c.c. contained only 0.53 c.c. immediately after dark, and only 0.23 c.c. an hour later. Water free from organisms which contained only 0.23 c.c. of oxygen contained 1.45 c.c. after addition of *Euglena viridis* and two hours' exposure to light.

N. H. J. M.

Formation of Oxalic Acid by *Aspergillus Niger*. CARL WEHMER (*Centr. Bakt. Par.*, 1906, ii, 15, 688-690).—A reply to Charpentier (*Abstr.*, 1905, ii, 749. Compare Wehmer, *ibid.*, 1892, 230).

N. H. J. M.

Action of Aluminium Salts on Germination. H. MICHEELS and P. DE HEEN (*Bull. Acad. roy. Belg.*, 1905, 520-523. Compare *Abstr.*, 1905, ii, 431).—Janano has shown that the addition of small quantities of ammonium alum to soil leads to an increased development in plants grown therein (*Bull. Coll. Agr. Tōkyō*, 1905, 6, 429). This observation has been extended by the authors to the germination of seeds (wheat) in aqueous solutions. Under these conditions they find that the addition of soluble aluminium salts is injurious, whereas the addition of alumina or kaolin is beneficial, especially if the solution in which the seeds are germinating is traversed by an electric current carried in by aluminium electrodes (compare this vol., ii, 115).

T. A. H.

Influence of Aluminium Ions on Lupin Seedlings. H. D. HOUSE and WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1905, xix-xx; *Amer. J. Physiol.*, 15).—Little or no effect on the growth of seedlings is produced by various aluminium salts at a concentration of $m/65536$. In concentrations greater than this, growth is usually inhibited; in smaller concentrations down to $m/2097152$, growth is usually accelerated.

W. D. H.

Action of Phosphoric Acid on Higher Plants and a New Nutritive Solution. C. VON DER CRONE (*Bied. Centr.*, 1906, 35, 30-33; from *Inaug. Diss. Bonn*, 1904, and *Naturw. Rundsch.*, 1905, 264).—In water-culture experiments with different plants, it was found that when phosphoric acid was absent the root development was retarded, and the roots were yellow when iron (as sulphate) was present, but not in absence of iron. When a phosphate was added, the iron was precipitated and its injurious action prevented; the plants then suffered from chlorosis.

Good results were obtained when ferrous phosphate and tribasic calcium phosphate were added to the solution. With dibasic calcium phosphate, the plants were chlorotic and the root development more restricted.

The assumption that the constituents of nutritive liquids should all

be in solution is incorrect. The solution recommended contains, per litre, potassium nitrate (1 gram), calcium sulphate, magnesium sulphate (each 0.5 gram), ferrous phosphate, and tertiary calcium phosphate (each 0.25 gram).
N. H. J. M.

Respiration of Flowers. MAIGE (*Compt. rend.*, 1906, 142, 104—106).—In most plants the intensity of respiration, in relation to the fresh weight and the carbon dioxide liberated, decreases regularly from the commencement to the end of flowering. In a very few cases, however, there is an increase during the development of the flower.

N. H. J. M.

Composition of the Liquids which Circulate in Plants ; Variations of the Nitrogen in the Leaves. GUSTAVE ANDRE (*Compt. rend.*, 1906, 142, 106—108).—Determinations of total nitrogen, nitrogen as nitrates, and phosphoric acid were made in the expressed sap of the leaves of a quickly growing annual (*Papaver somniferum*) from June 14 to July 10, and of *Pyrethrum balsamita* from May 3 to June 30.

The total nitrogen in the sap of the leaves of *Pyrethrum* diminished from 0.103 to 0.068 per cent., whilst the phosphoric acid increased. In the case of *Papaver* there was a slight increase in the nitrogen, whilst the phosphoric acid was highest at the second date (June 28). The disappearance of the nitrogen as nitrates was much more rapid in the case of *Papaver* than in *Pyrethrum*.

N. H. J. M.

Migration in the Leaves of Acer Negundo. B. SCHULTZE (*Bied. Centr.*, 1906, 35, 35—37; from *Verhandl. Ges. deut. Naturforsch. Aerzte*, '76, ii, 175).—The increase in the weight of leaves under the influence of light is not exclusively due to starch production, the amounts of proteids and other substances being also increased.

Leaves are able to assimilate carbon to the end, whilst the power of producing proteids gradually diminishes—so that finally the leaf becomes poor in the more readily soluble proteids. At the same time, the tissues become thickened, and fat accumulates owing to diminished oxidation. The leaf has now become useless and falls off.

N. H. J. M.

Examination of Aethusa Cynapium. FREDERICK B. POWER and FRANK TUTIN (*J. Amer. Chem. Soc.*, 1905, 27, 1461—1476).—This investigation was made with entire fresh plants of *Aethusa Cynapium* (fools' parsley) collected near London during July and August. The material was found to contain an *essential oil* which has a rather unpleasant odour, is colourless when first distilled, but rapidly becomes dark brown, and is present to the extent of 0.015 per cent. of the weight of the fresh plant. A mixture of resinous substances was extracted, equivalent to 0.8 per cent. of the weight of the fresh plant, from which were isolated a small quantity of pentatriacontane, melting at 74°, and a crystalline *alcohol* which melts at 140—141°, has $[\alpha]_D - 35.7^\circ$, and is either an isomeride of phytosterol or a lower homologue. When the resin was fused with potassium hydroxide,

formic, butyric, and protocatechuic acids were produced. Other constituents of the plant are *d*-mannitol, *i*-dextrose, and amorphous colouring matter. A small quantity of a volatile *alkaloid* was isolated which is present only to the extent of about 0.0003 per cent. The physical and chemical properties of this alkaloid and its physiological action indicate that it is probably either coniine or a mixture of bases such as that yielded by *Conium maculatum*. E. G.

Carbohydrates from Lichens A. ULANDER and BERNHARD TOLLENS (*Ber.*, 1906, **39**, 401—409. Compare Müller, *Abstr.*, 1905, ii, 648).—The lichens are divided into the two following groups: I. Group of Iceland Mosses, including *Cetraria islandica*, *Evernia prunastra*, *Usnea barbata*, *Cornicularia aculeata*, and the mould *Bulgaria inquinans*. Amorphous compounds of the type of lichenin, everniin, and a similar product from *Usnea* are obtained when these lichens are boiled with water and the extract precipitated with alcohol. When hydrolysed, these products yield dextrose. The lichens when hydrolysed with 5—6 per cent. sulphuric acid, after extraction with hot water, yield large quantities of dextrose and comparatively little *d*-mannose and *d*-galactose.

II. Group of Reindeer Mosses, including *Cladonia rangiferina*, *Stereocaulon pascale*, *Peltigera aptosa*. These yield no amorphous products of the type of lichenin, and the residues left after extraction with hot water are less readily hydrolysed. The chief products of hydrolysis are *d*-mannose and *d*-galactose together with small amounts of dextrose.

Both groups contain pentosans and methylpentosans. The residue left after hydrolysis consists essentially of cellulose. J. J. S.

Fruit Juice Statistics. HEINRICH LÜHRIG, ADOLF BEYTHIEN, L. WATERS, ADOLF JUCKENACK, F. MORSCHÖCK, and A. and M. DOMINKIEWICZ (*Zeit. Nahr. Genussm.*, 1905, **10**, 713—744).—Tabulated results of the analyses of numerous samples of fruit juices made during the year 1905 are given. The samples include currant, cherry, bilberry, raspberry, blackberry, and strawberry juices.

W. P. S.

Importance of Asparagine and Lactic Acid for the Feeding of Non-carnivorous Animals. OSCAR KELLNER (*Bied. Centr.*, 1906, **35**, 45—48; from *Verhandl. deut. Naturforsch. Aertze*, **76**, ii, 145).—The results of experiments with sheep indicated that lactic acid is simply oxidised and produces only heat which is not required. With a low proteid food, asparagine indirectly economises a small amount of proteid.

N. H. J. M.

Manurial Experiments with Lime. M. HOFFMANN (*Bied. Centr.*, 1906, **35**, 12—21; from *Arb. deut. Landw.-ges.*, Heft. 106).—The results of five years' experiments in different places showed that as a rule application of lime is beneficial.

As regards the effect of lime on leguminous plants, most of the

experiments failed owing to dry weather. In some cases, nowever, very marked results were obtained, even yellow lupins being benefited by lime in conjunction with kainite.

N. H. J. M.

Analytical Chemistry.

Calculations in Volumetric Analysis. EMIL PETERSEN (*Zeit. anal. Chem.*, 1906, **45**, 14—18).—Formulæ are given for facilitating the calculation in volumetric analysis when solutions only approximately normal are at disposal. L. DE K.

A New Indicator. JAMES ROYLE WOODS (*J. Soc. Chem. Ind.*, 1905, **24**, 1284).—Twenty-three grams of the compound produced by combining 1 mol. of diazotised *p*-nitroaniline with 1 mol. of 2-amino- α -naphthol-5:7-disulphonic acid are boiled with 5.5 grams of benzaldehyde, 100 grams of hydrochloric acid (18° B.), and 900 grams of water for fifteen minutes. The compound which crystallises out on cooling is a very delicate indicator for acid and alkali titrations. In the presence of acid, the compound is colourless, and in the presence of alkali intensely orange. It is sensitive to carbon dioxide.

W. P. S.

Use of the Rotating Anode and Mercury Cathode in Electroanalysis. II. LILY G. KOLLOCK and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1905, **27**, 1527—1549).—A lengthy paper profusely illustrated with curves, but unsuitable for condensation.

Further experiments with the following metals are communicated: cadmium, silver, mercury, bismuth, cobalt, tin, and iron, also mixtures of the latter with uranium, aluminium, thorium, lanthanum, praseodymium, neodymium, cerium, and zirconium.

When electrolysing chlorides, covering the liquid with a layer of toluene is recommended. L. DE K.

Use of Hydrogen Peroxide in the Quantitative Separation of the Halogens. PAUL JANNASCH and FR. ZIMMERMANN (*Ber.*, 1906, **39**, 196—197).—The haloid mixture is distilled from a flask containing water (120—150 c.c.), glacial acetic acid (15 c.c.), and 30 per cent. hydrogen peroxide (3 c.c.) and the iodine collected in Péligré tubes containing water, ammonium hydroxide, and hydrazine sulphate. The contents of the tubes are poured into a beaker, mixed with concentrated nitric acid (30—40 c.c.), and the iodide precipitated as silver iodide. Chlorine and bromine do not pass over with the iodine.

J. J. S.

A Modified Method for Standardising Iodine Solutions. SIGMUND METZL (*Zeit. anorg. Chem.*, 1906, **48**, 156—161).—Iodine

solutions can be standardised with antimonyl potassium tartrate; the pure crystallised salt or the anhydrous salt, dehydrated at 100° , is dissolved in water in the presence of a little tartaric acid, the solution is rendered alkaline with sodium carbonate in the presence of phenolphthalein, and carbon dioxide passed in until the red colour disappears; the titration is then carried out with iodine and starch in the usual way. Comparison of the results with those obtained by estimating the iodine with sodium thiosulphate standardised against potassium dichromate show that the method is accurate. It is to be recommended when the iodine solution is to be used for the estimation of antimony compounds.

G. S.

Estimation of Sulphur in Roasted Zinciferous Pyrites and similar Ores. GEORG LUNGE and R. STIERLIN (*Zeit. angew. Chem.*, 1906, 19, 21—27).—The Watson-Lunge method (roasting with sodium hydrogen carbonate and titrating the excess of alkali) does not work satisfactorily with zinciferous pyrites. The following modification of the process is recommended.

3.206 grams of the sample are mixed with 2 grams of sodium-hydrogen carbonate of known titre and 2 grams of potassium chlorate and heated gradually to redness, but not to fusion, in a covered nickel crucible for twenty minutes. When cold, the mass is extracted with a solution of pure sodium chloride and the undecomposed alkali titrated with normal hydrochloric acid, using methyl-orange as indicator.

For roasted ores containing 6 or more per cent. of sulphur, the following mixture is recommended: 1.603 grams of sample, 2 grams of sodium-hydrogen carbonate, 4 grams of potassium chlorate, and 2 to 3 grams of pure iron oxide. In the case of unroasted ores, 0.3206 gram of sample, 2 grams of sodium-hydrogen carbonate, 2 grams of potassium chlorate, and 2 grams of iron oxide are taken. L. DE K.

Iodometric Estimation of Sulphates. MAX SCHOLTZ (*Arch. Pharm.*, 1905, 243, 667—672).—Solutions of barium chloride and potassium chromate are prepared equivalent to $N/10$ sodium thio-sulphate solution. The substance to be examined is dissolved in water in a 150 (or 125) c.c. graduated flask and heated; 50 (or 25) c.c. of the barium solution are added and the mixture is warmed for a time on the water-bath. It is then filtered through a dry filter into a dry vessel. Of the filtrate, 100 c.c. are mixed with 50 (or 25) c.c. of the chromate solution and filtered into a dry vessel. (In both these filtrations, the small quantity which first passes through the filter is rejected.) Of the second filtrate, 100 c.c. are mixed with 10 c.c. of 10 per cent. aqueous potassium iodide and 10 c.c. of 15 per cent. hydrochloric acid, and the iodine liberated is titrated with the thio-sulphate solution. If a c.c. of this are used, the weight of SO_4 present is $0.0032 (2.25a - 25)$ [or $0.0032 (1.5625a - 6.25)$]. In only one of four experiments did the error exceed 1 per cent. of the total amount estimated.

C. F. B.

Assay of Sodium Thiosulphate. G. HÜBENER (*Chem. Zeit.*, 1906, 30, 58—60).—Direct titration with iodine is inadmissible when the sample contains sulphite, as this absorbs twice as much iodine as the thiosulphate. By titrating, however, a certain volume of the solution directly with iodine and then also titrating the sulphurous acid expelled by boiling with dilute sulphuric acid, it is possible by calculation to get at the true amount of thiosulphate.

A mixture of thiosulphate, sulphite, sulphate, and sulphide is best tested as follows: an aliquot part of the solution is digested with cadmium carbonate, and the cadmium sulphide so obtained is oxidised with bromine dissolved in hydrochloric acid and precipitated with barium chloride. The filtrate is made up to a definite bulk and three equal portions are pipetted off. (1) Is titrated with iodine. (2) Is distilled with addition of sulphuric acid in a current of carbon dioxide, and the sulphurous acid evolved is passed through standard iodine solution, which is then finally titrated with thiosulphate. From the results, the sulphite and thiosulphate are calculated. (3) Is oxidised with excess of iodine solution and precipitated with barium chloride, and after allowing for the sulphate yielded by the sulphite, the balance of barium sulphate is calculated into sodium sulphate. For apparatus employed and details of calculation, the original article should be consulted.

L. DE K.

Reducing Action of Hydrogen. II. Estimation of Traces of Arsenic by the Marsh-Berzelius Method, and the "Insensitiveness" of Zinc. ALFRED C. CHAPMAN and HERBERT D. LAW (*Analyst*, 1906, 31, 3—16. Compare Abstr., 1905, ii, 695).—It is shown that the reducing efficiency of hydrogen obtained as the result of the interaction of metals and acids is dependent on a number of factors, both chemical and physical, and that amongst these factors the question of "potential" and "supertension" plays a very prominent and important part. In the case of the solution of pure zinc in sulphuric acid in the presence of arsenious oxide there will be still left in solution, after the action has been allowed to take place until as much hydrogen arsenide has been driven off as it is possible to obtain, a minute quantity represented by M_{AsH_3} , which is proportional to the product $M_{\text{As}} \cdot M_{\text{H}}$ and is influenced by the potential of the various active ions. In the extremely dilute solutions employed, the equation becomes $M_{\text{AsH}_3} \rightleftharpoons K \cdot \text{As} P_{\text{H}}$, where As represents the amount of unreduced arsenious oxide and K a constant factor. Numerous experiments are described on the effect of the addition of various metals and salts to the evolution part of the Marsh-Berzelius apparatus.

W. P. S.

Use of Platinum and Copper as "Accelerators" in Marsh's Apparatus. ZOLTAN DE VAMOSSY (*Bull. Soc. chim.*, 1906, [iii], 35, 24—28).—The author agrees with Mai and Hurt (Abstr., 1905, ii, 61) that copper may be used as an "accelerator" in Marsh's arsenic test, and points out that Gautier's view, that when copper is employed in this way part of the arsenic is converted into copper arsenide and is lost, probably applies only to cases where comparatively large quantities of arsenic are present. The results of a number of experi-

ments carried out in a modified form of Bertrand's apparatus (Abstr., 1904, ii, 85) are given, showing that although platinum is a better "accelerator" than copper the latter gives quite as accurate results.

T. A. H.

Occurrence of Arsenic in Wines. HARRY D. GIBBS and C. C. JAMES (*J. Amer. Chem. Soc.*, 1905, 27, 1484—1496).—The authors have investigated 329 samples of wine and found arsenic in 38 samples; the largest quantity found was, however, only 1 part in 20,000,000. Its presence is probably due to the use of arsenical sprays on the vines, in the use of impure sulphur for sulphuring the wine, and it may also have been derived from the lead shot used in cleaning the bottles.

Fifty c.c. or more of wine are made alkaline with calcium hydroxide suspended in water, evaporated to dryness, and gently burnt to ash. The ash, which has retained all the arsenic, is then tested by the "mirror method" in a Marsh apparatus.

L. DE K.

Estimation of Carbon Monoxide in Air by means of Iodine Pentoxide. ALBERT LÉVY and ADRIEN PÉCOUL (*Compt. rend.*, 1906, 142, 162. Compare Abstr., 1905, ii, 203; Jaubert, this vol., ii, 125).—Gautier has shown (Abstr., 1898, ii, 640; 1901, ii, 232; this vol., ii, 125) that even at 35° the oxidation of acetylene by iodine pentoxide is incomplete, only between 0.1 and 0.2 of the acetylene being oxidised when it is present in the air in the proportion of 10 or 20 parts per 10,000 volumes. The authors find that the fraction of the acetylene oxidised diminishes as the dilution increases and that air containing 1 part of acetylene in 10,000 volumes does not produce any coloration in chloroform after passing over iodine pentoxide, whilst the same proportion of carbon monoxide produces an intense coloration.

M. A. W.

Assay of Silver Coins in Bulk. COPIUS HOITSEMA (*Zeit. anal. Chem.*, 1906, 45, 1—13).—The well-known wet assay of silver may be rendered still more delicate by operating on a much larger quantity of the sample than usual, say 5 grams. This necessitates the use of larger Stas pipettes for measuring the sodium chloride solution. For the various precautions to be observed in the weighings, &c., and for a more effectual way of getting trustworthy average samples of silver from the coins, the original article and illustrations should be consulted.

L. DE K.

Estimation of Zinc in Zinc-aluminium Alloys. RICHARD SELIGMAN and F. J. WILLOTT (*J. Soc. Chem. Ind.*, 1905, 24, 1278—1279).—About 0.5 gram of the alloy is dissolved in 25 c.c. of 25 per cent. sodium hydroxide solution. The solution is then diluted to a volume of 300 c.c. with boiling water and the clear liquid decanted off; any residue is dissolved in hydrochloric acid, reprecipitated with sodium hydroxide in excess, filtered, and the filtrate added to the main solution. Hydrogen sulphide is now passed through the latter, the stream of gas being stopped when a skin begins to form at the point where the bubbles of gas burst, showing that alumina is being precipitated with the zinc sulphide. The precipitate is collected

on a filter and dissolved in 8 c.c. of hydrochloric acid, washing the precipitate being unnecessary. The filter is, however, carefully washed after dissolving the precipitate, and the solution obtained titrated with potassium ferrocyanide solution after the addition of 5 grams of ammonium chloride and diluting to 250 c.c. with boiling water. Uranium nitrate or ammonium molybdate may be used as indicator.

W. P. S.

Volumetric Estimation of Lead as Iodate. L. MOSER (*Chem. Zeit.*, 1906, 30, 9—10).—The process, which is particularly suited for sugar of lead, consists in adding a known quantity of potassium iodate and titrating the excess of iodic acid in a portion of the filtrate with sodium thiosulphate after adding potassium iodide and dilute sulphuric acid. The difference in iodic acid represents the insoluble lead iodate.

. If, before acidifying with sulphuric acid, any iodine should be liberated, this may be at once titrated, as it represents the free acid of the sample.

L. DE K.

Volumetric Estimation of Lead as Iodate. ERWIN RUPP (*Chem. Zeit.*, 1906, 30, 37).—A claim for priority (see preceding abstract).

L. DE K.

Estimation of Nickel. H. CORMIMBŒUF (*Ann. Chim. anal.*, 1906, 11, 6—8).—The metal or alloy is dissolved in acid and the solution treated with hydrogen sulphide and filtered. The filtrate is boiled to expel the hydrogen sulphide, and any iron present is precipitated by ammonia. After collecting the precipitate of ferric hydroxide on a filter, it is dissolved in a little hydrochloric acid, reprecipitated by ammonia, and again brought on to a filter. The united filtrates and washings are now treated with a current of hydrogen sulphide and the nickel sulphide collected on a filter. During the filtration, the filter must be kept full. The precipitate is washed with cold water, then with alcohol, and finally ignited together with the filter in a porcelain crucible. The heat must not be excessive at the commencement of the ignition, but at the end may be increased to bright redness. The contents of the crucible may be stirred during the ignition in order to facilitate the conversion of the sulphide into oxide.

W. P. S.

Use of Ammonium Persulphate in the Estimation of Chromium in Steel. HARRY E. WALTERS (*J. Amer. Chem. Soc.*, 1905, 27, 1550—1553).—1.25 grams of the sample are heated with 35 c.c. of dilute sulphuric acid (1:5), and when all is dissolved the iron and any carbonaceous matter are oxidised by means of ammonium persulphate; the whole is diluted to 100 c.c. and mixed with 40 c.c. of silver nitrate solution (4 grams in 1 litre). Five to seven grams of slightly moist ammonium persulphate are now added and the mixture is heated to boiling; after boiling for another five minutes to destroy the excess of the reagent, the whole is allowed to cool and made up to 500 c.c.

Four hundred c.c. of the solution are now mixed with a known volume of ferrous sulphate solution (22.5 grams of ferrous ammonium sulphate and 50 c.c. sulphuric acid in 1 litre), and the excess of iron is then titrated with standard permanganate (1.82 grams in 1 litre). The number of c.c. used subtracted from the check represents chromium and manganese.

The remaining 100 c.c. are titrated with standard sodium arsenite until the colour is bright yellow. This solution has been previously checked with a chrome steel containing a known percentage of manganese. The number of c.c. of permanganate used by the chromium is found by deducting from the total the calculated number of c.c. corresponding with the manganese found by the arsenic titration.

L. DE K.

Quantitative Electrolytic Separation of Tin from Nickel and Cobalt and of Copper from Antimony. NICOLAI A. PUSCHIN and R. M. TRECHZINSKY (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 828—833).—Contrary to what would be expected from theoretical considerations, tin, cadmium, and zinc can be precipitated electrolytically from acid, and cobalt and nickel from neutral solutions. On the basis of these results, the authors have devised the following method for separating tin from nickel or cobalt. To a neutral solution of the two metals, about 3 grams of ammonium oxalate are added for every gram of tin present, and about 3 grams of oxalic acid for every gram of nickel (or cobalt), and 15—20 grams per gram of tin. Through the liquid containing the precipitated nickel (or cobalt) oxalate, a current is kept passing at a voltage not less than 2.2 until the whole of the tin is deposited, each gram of tin requiring six to seven ampere-hours. The liquid is then heated with concentrated ammonia solution to dissolve the nickel (or cobalt) oxalate and the nickel (or cobalt) determined by Oettel's method (*Zeit. Elektrochem.*, 1894—1895, **1**, 192—194).

On dissolving an alloy of copper and antimony in nitric acid, the latter metal is precipitated as metantimonic acid, and if the liquid is diluted with water and submitted to the action of the electric current, only the copper is deposited at voltages less than 2.05. When all the copper has been removed from the solution, the metantimonic acid is dissolved in sodium sulphite, sodium hydroxide being then added to the solution thus obtained and the antimony estimated by Classen's method.

T. H. P.

Gravimetric Estimation of Bismuth as Phosphate and its Separation from Cadmium and Copper. L. MOSER (*Zeit. anal. Chem.*, 1906, **45**, 19—26).—The solution of bismuth nitrate, which should not be too strong and should not contain much free acid, is heated nearly to boiling and a *N/5* solution of ammonium phosphate is added slowly whilst stirring until a slight excess is present. The bismuth phosphate (BiPO_4) is collected, washed with hot water, and finally ignited, the filter being burnt separately. The results are very satisfactory.

In the presence of moderate amounts of copper or cadmium, the

bismuth solution is first mixed with 50—100 c.c. of *N*/10 nitric acid, heated to boiling, and precipitated with ammonium phosphate as before. The clear liquid is carefully poured off, and the precipitate is boiled with 50—100 c.c. of *N*/10 nitric acid, which completely removes any co-precipitated cadmium or copper. A little bismuth phosphate which is also dissolved is, however, reprecipitated completely by adding 10—20 c.c. of ammonium phosphate solution.

L. DE K.

Supposed Sources of Error in the Simplified Method of Elementary Analysis. MAXIMILIANO DENNSTEDT (*Zeit. anal. Chem.*, 1906, 45, 26—31. Compare Abstr., 1903, ii, 103; 1905, ii, 202, 651).—A reply to the criticisms of Hermann (Abstr., 1905, ii, 767).

L. DE K.

New Method for the Elementary Analysis of Organic Compounds. ORESTE CARRASCO (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 608—612).—The method devised by the author admits of the combustion of an organic substance, including the weighings, being completed in an hour. The apparatus, for the details and sketch of which the original paper must be consulted, consists of a piece of combustion tubing 20 cm. long and 2 cm. in external diameter, one end of which is sealed and blown out so as to form a slight bulb. The other end of this combustion tube is closed by a double-bored cork, through which pass: (1) a piece of infusible glass tubing about 23 cm. long and 5 mm. in outside width, reaching nearly to the bulb of the combustion tube; this inner tube is surrounded at its upper part by a piece of platinum foil furnished with a small hook, to which is attached the end of a platinum iridium wire 0.2 mm. thick wound round the exterior of the inner tube and attached by a hook to a straight platinum wire 1.5—2 mm. thick, passing up through the interior of the tube; (2) a short piece of glass tubing sealed at the lower end, just above which is a lateral opening, and bent at the upper end to allow of the products of combustion being conducted to the absorption apparatus. Powdered copper oxide is placed in the bulb of the combustion tube and, after the inner tube has been placed in position, a current of 3 amperes at a voltage of 20 is passed through the platinum wire spiral and the copper oxide is heated by means of a small Bunsen burner. After about three minutes, the heating is interrupted and a current of oxygen passed through the combustion tube by way of the inner tube. When the tube is cool and the absorption apparatus arranged in position, the weighed substance to be analysed is dropped on to the copper oxide, with which it is mixed by shaking. The tube is then heated as before, a moderately rapid stream of oxygen being maintained. With a difficultly volatile compound, the copper oxide must be cautiously heated from time to time.

The method gives good results and can be applied to compounds containing ammoniacal nitrogen. If the substance contains the nitro-group, the products of combustion must be passed through a U-tube filled with lead peroxide heated at 160—180° before they traverse the absorption apparatus.

T. H. P.

New Method for estimating the Carbon and Hydrogen in Organic Substances by means of Electrical Incandescence. ORESTE CARRASCO and GIUSEPPE PLANCHER (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 613—618).—The authors describe an apparatus and method differing only in certain details from that described in the preceding abstract.

T. H. P.

Some Uses of Carbon Tetrachloride in the Laboratory. EDMUND GRAEFE (*Chem. Rev. Fett. Harz.-Ind.*, 1906, 13, 30—32).—Carbon tetrachloride is particularly suitable as a solvent for paraffin in the estimation of the iodine number of the latter. Owing to the greater solubility of paraffin in carbon tetrachloride, there is no danger of the paraffin being precipitated on the addition of the alcoholic reagents, as is very often the case when chloroform is used as a solvent. Hard paraffin can also be precipitated fractionally from its solution in carbon tetrachloride by the addition of alcohol, and the presence of small quantities of paraffin with a higher melting point in an apparently homogeneous product can thus be detected.

W. P. S.

Behaviour of Gaseous Hydrocarbons towards Magnesium at a Red Heat. ALEXANDER P. LIDOFF and M. I. KUSNEZOFF (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 940—943).—On passing methane, ethane, ethylene, or acetylene over magnesium heated to redness, practically the whole of the carbon of the hydrocarbon is absorbed by the heated metal, whilst the hydrogen passes on. On the basis of these results, the authors suggest a process for investigating furnace gases. These gases contain carbon dioxide, carbonic oxide, oxygen, hydrocarbons, hydrogen, and nitrogen, and, by the ordinary methods of analysis, a residue is obtained consisting of the hydrocarbons, hydrogen, and nitrogen. If this residue is heated with magnesium, the gas remaining consists of the total hydrogen, whilst the increase in weight of magnesium represents the carbon and nitrogen. The latter can easily be determined by Kjeldahl's method after absorption by the magnesium.

T. H. P.

Estimation of Naphthalene in Coal Gas. C. J. DICKENSON-GAIR (*J. Soc. Chem. Ind.*, 1905, 24, 1279—1280).—A measured volume of the gas, usually from 3 to 6 cb. ft., is passed at the rate of 1 cb. ft. per hour through two Woulfe's bottles, each containing about 175 c.c. of acetic acid of sp. gr. 1.044, and then through a small Woulfe's bottle containing 150 c.c. of concentrated picric acid solution. If the gas contains ammonia, it must be passed through a wash-bottle containing hot oxalic acid solution before entering the Woulfe's bottles. At the end of the experiment, the acetic acid and the picric acid from the bottles are mixed in a flask and about 500 c.c. of concentrated picric acid solution are added. The naphthalene picrate which separates is collected on a filter, dried in a warm room, and weighed. The method is shown to be trustworthy and the results obtained agree with those found by Colman and Smith's method (*Abstr.*, 1900, ii, 372).

W. P. S.

Estimation of Small Quantities of Chloroform ; its Estimation : I in Air, II in Blood or in an Aqueous Liquid. MAURICE NICLOUX (*Compt. rend.*, 1906, 142, 163—165).—Small quantities of chloroform (0.1 to 0.004 gram) can be estimated by heating for one hour in a reflux apparatus 60 c.c. of alcohol containing the chloroform, with 10 c.c. of a 10 per cent. alcoholic solution of potassium hydroxide, adding 15 c.c. of water to the cooled liquid, neutralising in the presence of phenolphthalein, and titrating the chlorine with *N*/20 silver nitrate solution. The results show a constant error of 1.5 to 2 per cent. (compare Saint-Martin, *Abstr.*, 1888, 570). The method can be applied (1) to the estimation of the amount of chloroform in air by first absorbing the chloroform in alcohol contained in a series of bulbs through which the air is aspirated. (2) To the estimation of the chloroform in blood or in any other aqueous liquid by adding to the suspected liquid five times its volume of alcohol containing 0.25 gram of tartaric acid, and distilling one-third of the total liquid into 10 c.c. of alcohol, which is then treated as above.

M. A. W.

Ergosterol. D. OTTOLENGHI (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 697—705).—As obtained by Bömer's method (*Abstr.*, 1899, ii, 191) from the fat of rye, ergosterol contains a small amount of a *product* which forms small, white flocks melting at 60—61° and is non-saponifiable, but the nature of which is unknown. The ergosterol prepared by the author possesses the properties given by Tanret (*Abstr.*, 1889, 407). Analysis of ergosterol gives numbers corresponding with the formula $C_{24}H_{40}O + H_2O$ or possibly $C_{25}H_{42}O + H_2O$, and this result is confirmed by the cryoscopic behaviour of its acetyl derivative in benzene solution ; it must hence be regarded as a lower homologue of cholesterol. It has $[\alpha]_D - 89.5^\circ$ at 15°.

The following reactions are given as characteristic of the sterols: (1) if a concentrated chloroform solution of ergosterol is shaken with an equal volume of concentrated sulphuric acid, after some time the liquid separates into an upper layer, which contains the chloroform and has a yellow colour with a faint rose tint, and a lower layer, which has an intense yellowish-brown colour and a green fluorescence. Under the same conditions cholesterol gives a blood-red coloration to the chloroform, and, of the phytosterols, some behave like cholesterol whilst others yield a bluish-red or violet coloration. (2) If the chloroform solution of ergosterol is shaken with only one-half its volume of concentrated sulphuric acid, the chloroform becomes pale red and the sulphuric acid wine-red ; on addition of two drops of acetic anhydride, the chloroform changes to a reddish-violet colour. With cholesterol, after the addition of acetic anhydride, the chloroform is coloured carmine and the sulphuric acid blood-red. (3) On adding dilute sulphuric acid drop by drop to a solution of ergosterol or cholesterol in acetic anhydride, the liquid becomes coloured at first red, but changes rapidly to violet and finally to green. (4) If excess of acetyl chloride and a fragment of zinc chloride are added to an acetic anhydride solution of ergosterol, the liquid is immediately coloured red, then pale green, and finally yellowish-brown with a yellowish-

green fluorescence. In the cold, cholesterol does not give this reaction, but on heating it gives a coloration similar to that of eosin. (5) If to an absolute alcoholic solution of ergosterol, or of one of the cholesterol or phytosterols, a few drops of δ -methylfurfuraldehyde and an equal volume of concentrated sulphuric acid are added, a red ring is formed at the surface of separation of the two liquids. If the liquid is shaken and cooled, it all turns red and exhibits a well-defined absorption band in the bluish-green part of the spectrum. (6) On adding to 10 drops of trichloroacetic acid solution (9 parts of acid to 1 of water) about 1 mg. of ergosterol or cholesterol, the colour of the liquid changes after one hour to pale violet and after twelve hours to an intense reddish-violet. If, however, the mixture is at once boiled, the liquid becomes red at first and turquoise-violet after twelve hours. (7) A trace of ergosterol or cholesterol, moistened on platinum foil with a drop of nitric acid and allowed to evaporate, leaves a yellow spot, which becomes orange-red when treated with ammonia.

T. H. P.

Volumetric Estimation of Pentoses. ADOLF JOLLES (*Ber.*, 1906, 39, 96—97).—The pentose (0.2—1 gram) is treated with 200 c.c. of hydrochloric acid of sp. gr. 1.06 and a current of steam passed through the solution until the formation of furfuraldehyde is complete, as shown by Bial's reagent, a further quantity of 100 c.c. of hydrochloric acid being added during the distillation. An aliquot part of the distillate, which contains about 1.1 per cent. of hydrogen chloride, is neutralised and a measured excess of potassium hydrogen sulphite added, which forms the additive compound with the furfuraldehyde; after two hours, the excess of potassium hydrogen sulphite is titrated with iodine solution. As the reactions take place quantitatively, 1 mol. of potassium hydrogen sulphite is equivalent to 1 mol. of pentose or to 2 mols. of iodine.

G. Y.

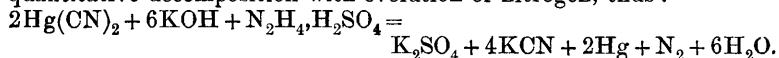
New Method for the Estimation of Reducing Sugars. D. SIDERSKY (*Ann. Chim. anal.*, 1906, 11, 8).—The author confirms the accuracy of Lavallo's method (*Abstr.*, 1905, ii, 558).

W. P. S.

Two New Methods for the Estimation of Dextrose. BORIS GLASSMANN (*Ber.*, 1906, 39, 503—508).—The indirect volumetric method described for the estimation of dextrose depends on its quantitative oxidation to saccharic acid either by alkaline mercuric cyanide or by potassium mercuri-iodide, according to the equations: $C_6H_{12}O_6 + 3Hg(CN)_2 + 6KOH = C_6H_{10}O_8 + 4H_2O + 6KCN + 3Hg$ and $C_6H_{12}O_6 + 3HgI_2 + 2KI + 6KOH = C_6H_{10}O_8 + 4H_2O + 8KI + 3Hg$. The sugar solution is added to a boiling solution of alkaline mercuric cyanide or of potassium mercuri-iodide; the mercury which separates is filtered, dissolved in concentrated nitric acid, and estimated according to Rupp and Krauss' method (*Abstr.*, 1902, ii, 475. Compare also Cohn, *Abstr.*, 1902, ii, 50).

Dextrose may also be estimated by a gas volumetric method as follows. If an alkaline solution of mercuric cyanide or of potassium

mercuri-iodide is warmed with a hydrazine salt, the latter undergoes quantitative decomposition with evolution of nitrogen, thus :



If the nitrogen evolved is measured, the percentage of mercury in the solution may be determined. The sugar solution is treated with a definite excess of a titrated mercuric cyanide solution according to the first method described and the excess of mercury present determined by means of hydrazine sulphate. The amount of sugar in the original solution may then be calculated. A. McK.

Colour Reactions of Important Sugars. NICOLAAS SCHOORL and P. C. J. VAN KALMTHOUT (*Ber.*, 1906, 39, 280—285).—The authors have examined the colour reactions described by Pinoff (*Abstr.*, 1905, ii, 865), and express doubts as to their value as characteristic tests.

W. A. D.

Estimation of the Free and Combined Tartaric Acid in Wine. A. HUBERT (*Ann. Chim. anal.*, 1906, 11, 1—5).—*Potassium Hydrogen Tartrate*.—One hundred c.c. of the wine are evaporated to a volume of about 5 c.c. and the residue placed aside for twelve hours; 3 c.c. of 40 per cent. alcohol are then added, and the crystals carefully brought on to a small filter and washed with successive small quantities of the alcohol, using not more than 20 c.c. altogether. The crystals are now dissolved in hot water and the solution titrated with *N*/10 sodium hydroxide, using phenolphthalein as indicator. The number of c.c. used multiplied by 0.188 gives the quantity of potassium hydrogen tartrate per litre of the wine, to which is added 0.02 gram to correct for the solubility of the crystals in the alcohol used for washing.

Free Tartaric Acid.—Ten drops of a 20 per cent. potassium bromide solution are added to 100 c.c. of the wine, and the process continued as described under potassium hydrogen tartrate. The difference between the result now obtained and that found previously is equivalent to the free tartaric acid in the wine, expressed as potassium hydrogen tartrate.

Tartaric Acid combined with Calcium, &c.—The difference between the alkalinity of the total ash of the wine and that of the soluble ash is equivalent to the tartaric acid combined with the alkaline earths.

W. P. S.

Comparison of the Estimation of Fat in Milk by Gottlieb's and Gerber's Methods and by Wollny's Refractometer. HANS SCHROTT-FIECHTL (*Milchw. Zentr.*, 1906, 2, 13—19).—Some 200 comparative results of estimations of fat in milk by these three processes are given, from which it is seen that all three yield trustworthy results, the agreement of the figures in every case being exceedingly close.

W. P. S.

Occurrence of Cholesterol and Lecithin in Milk and its Influence on the Estimation of Fat in Milk by Gottlieb's Method. MORITZ SIEGFELD (*Milchw. Zentr.*, 1906, 2, 1—5).—The

author has found from 0.0029 to 0.0036 per cent. of cholesterol and from 0.0079—0.0166 per cent. of lecithin in milk. These two substances pass into solution in the solvents employed in Gottlieb's method, and although their presence may be neglected in the case of full milks, with machine-separated milks the combined weight of cholesterol and lecithin constitutes an appreciable proportion of the fat obtained.

W. P. S.

Taint in Milk due to Contamination with Copper. JOHN GOLDING and ERNEST FEILMANN (*J. Soc. Chem. Ind.*, 1905, **24**, 1285—1286).—The presence of copper from a worn cooler caused the development of an "alkaline mealy" flavour in a milk supply, and from their experiments the authors find that copper is acted on by milk, especially in the presence of air, and that from 1 to 100 or more parts of the metal are dissolved per million parts of milk. Fresh milk when thus contaminated is very liable to develop the peculiar flavour in about eighteen hours. The flavour appears to be due in part to the development of certain micro-organisms in the presence of copper, the latter also checking the development of lactic ferments.

W. P. S.

Examination of Butter as regards its Purity. HEINRICH LÜHRIG (*Zeit. Nahr. Genussm.*, 1906, **11**, 11—20).—Of all the methods recently proposed for the detection of foreign fats in butter, not one, with the exception of Bömer's phytosterol acetate method (*Abstr.*, 1902, ii, 184), is infallible, owing to the difficulty of fixing "limits," the constants of each method allowing more or less foreign fat to be present before its presence is indicated with certainty. Bömer's method, however, besides detecting the presence of small percentages of foreign vegetable fats, also distinguishes between adulterated butter and that which is altered in its composition by the fat or oil contained in the food of the cow.

W. P. S.

Composition of the Fat of Pigs fed on Oil Meals. K. FARNSTEINER, K. LENDRICH, and PAUL BUTTENBERG (*Zeit. Nahr. Genussm.*, 1906, **11**, 1—8).—Analyses and physical tests are given of a number of lards obtained from pigs fed on potatoes, maize meal, cotton-seed meal, &c. The results show that a portion of the oil contained in these fodders is deposited in the body-fat of the animal, particularly in the case of maize meal. Lard from the pigs fed on cotton-seed meal gave a strong coloration with Halphen's reagent, but the melting point of the phytosterol acetate obtained from the fat according to Bömer's method (*Abstr.*, 1902, ii, 184) was in no case above 115.6°, showing that cotton-seed oil itself was not present.

W. P. S.

Surin Fat. JULIUS LEWKOWITSCH (*Analyst*, 1906, **31**, 2—3).—The fat examined came from Perak, Straits Settlements, and was probably derived from the seeds of a species of *Palaquium*. It yielded the following analytical results: free fatty acids, 43.2 per cent.; sp. gr. at 60°/60°, 0.9021; solidifying point, 48.9°; melting point, 56.1°; saponification number, 179.5; iodine number, 42.31; Reichert-Wollny number, 0.55; unsaponifiable matter, 4.54 per cent.

W. P. S.

Heat of Combustion of Beeswax and the Application of Calorimetric Methods to the Solution of certain Analytical Problems. NICOLAI W. SOKOLOFF (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 818—822).—Measurements made with samples of European, Asiatic, and American beeswax show that the heat of combustion of 1 gram of the yellow wax lies between 10,294 and 10,348 cal., the mean value being 10,312 cal. With these kinds, the ratio of the ester number to the acid number is 3.7—3.9. Beeswax from Macassar or Calcutta exhibits low values for the heat of combustion, namely, 10,107—10,294 cal. per gram, and also abnormal values, namely, 5.85—12.6, for the ratio between the ester and acid numbers. These differences are explained by the fact that the last two waxes are produced by a peculiar kind of bee, *Trigonas melipona*.

The heat of combustion of the paraffin and ceresin waxes has the mean value 11,234 cal. per gram.

Beeswax may be tested for the presence of paraffin or ceresin by boiling 4 grams of it with 25 c.c. of 5 per cent. alcoholic potassium hydroxide solution and 25 c.c. of 95 per cent. alcohol in a reflux apparatus. Incomplete saponification and solution of the whole of the wax indicates the presence of paraffin or ceresin, the amount of which can be calculated from the excess of heat of combustion of 1 gram of the wax over 10,312 cal.

T. H. P.

Use of Schiff's Reagent for the Detection of Formaldehyde in Milk. FRANZ UTZ (*Milchw. Zentr.*, 1906, 2, 12—13).—Schiff's reagent (magenta decolorised by sulphurous acid) is not to be recommended for the detection of formaldehyde in milk. It reacts with other aldehydes and is liable, under certain conditions, to give a reaction with milk containing no formaldehyde, especially when the milk and reagent are warmed together. The coloration, however, disappears on cooling.

W. P. S.

Detection, Estimation, and Rate of Disappearance of Formaldehyde in Milk. R. H. WILLIAMS and HENRY C. SHERMAN (*J. Amer. Chem. Soc.*, 1905, 27, 1497—1503).—When recently added, formaldehyde in milk may be readily detected by the well-known test with hydrochloric acid and ferric chloride, but after a few days this test may fail. In such a case it is still possible to detect this preservative by distilling the milk and applying to the distillate the well-known ring reaction with gallic and sulphuric acids.

For the estimation, 300 c.c. of milk are mixed with 3 c.c. of dilute sulphuric acid and distilled in a round-bottomed litre flask until 60 c.c. have passed over. The formaldehyde is then estimated by the potassium cyanide method. The quantity found represents about one-third of that originally added, that is to say, if the sample is fairly fresh.

A large number of experiments are given showing the rate of disappearance of formaldehyde from aqueous solutions and from milk. The rate of disappearance is not affected by allowing milk to become sour before adding the formaldehyde.

L. DE K.

Application of Methylene-blue to the Estimation of Sulphonic Derivatives of Aromatic Amino- and Hydroxy-compounds. WILHELM VAUBEL and E. BARTELT (*Zeit. Farb.-Ind.*, 1906, 5, 21—22).—Pellet and Garuti's process (*Abstr.*, 1904, ii, 794) of titrating methylene-blue with an acid dye can be applied to estimating certain amino- and hydroxy-sulphonic acids. There is, however, no definite connection between the number of sulphonic groups and the number of molecules of methylene-blue used in the inter-action, so that in most cases some other method of estimation is preferable.

W. A. D.

Adler's Benzidine Test for Blood-pigment. OTTO SCHUMM and C. WESTPHAL (*Zeit. physiol. Chem.*, 1905, 46, 510—514).—The test is a delicate one, but, like the guaiacum test, is given by other substances also. A further communication on the detection of blood-pigment in fæces is promised.

W. D. H.

New Method of estimating Rennin and the Behaviour of Human Gastric Juice under Normal and Pathological Conditions. LEON BLUM and ERNST FULD (*Chem. Centr.*, 1905, ii, 1742—1743; from *Berl. klin. Woch.*, 42, 107—118).—The strength of solutions of gastric juice or rennin is estimated by determining the concentration of the weakest solution which is still active. For this purpose, an emulsion is made by stirring and digesting 3 grams of Elsenberg's milk powder with nine times the quantity of water for one minute at 80°. A 20 per cent. solution of calcium chloride is added to the liquid, when cold, in the proportion of 2 c.c. to 98 c.c. of the milk. The milk, after settling or filtering, should be used as quickly as possible, but if kept for some time the calcium chloride should be added immediately before use. The filtered sample of gastric juice or rennet is added to the milk in the proportion of 0.5 c.c. to 4.5 c.c. of milk. The mixture is kept at a constant temperature of 15° for two hours and is then heated for five minutes at 37° in an Ostwald water-bath. The commencement of the action is readily detected, and the limits are, perhaps, more readily recognised than when ordinary milk is used. A solution containing 1 : 1000 may be assumed to be the lower limit of activity. If such a solution is inactive, preliminary trials should be made by allowing solutions containing 1 : 10, 1 : 100, and 1 : 1000 respectively to remain for five minutes at 37°. Since the lower limit obtained by the Morgenroth method is at least four times higher than that found by digesting the mixtures at 37°, it is advisable, in determining the exact limit, to begin with a solution of one-quarter the strength of that indicated by the preliminary test. It is not necessary to neutralise the gastric juice, since the acidity is negligible even in cases where the undiluted sample is required.

The gastric juice and other secretions of normal and of sick persons have been tested in this way; the total acidity and the quantity of free hydrochloric acid and pepsin were also determined. The presence of the pro-ferment, prochymosin, in gastric juice is very doubtful. For the purposes of diagnosis the determination of the quantity of rennet ferment is not more valuable than that of the pepsin, but a

knowledge of the extent of the decrease of the former is important. The rennin, however, may be more accurately estimated than the pepsin.

E. W. W.

Analytical Methods of Serum Pathology. WILFRED H. MANWARING (*J. Biol. Chem.*, 1906, 1, 213—218).—When serum and corpuscles are mixed together, analysis shows that there is sometimes more amboceptor than was originally present, in spite of the fact that amboceptor had been removed by the corpuscles. The interaction is therefore a more complex phenomenon than hitherto supposed, or else the method is wrong. Complex curves and formulæ have been calculated from the application of physical chemistry to problems of immunity under the erroneous assumption that numerous dissimilar fluids are analytically comparable to the few on which observations are made. In most cases, this assumption rests on no experimental basis.

W. D. H.

Microchemical Reaction of the Semen and its Application in Medico-legal Investigations. MICHELE BARBERIO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1905, [iii], 11, 156—168).—On adding to a drop of semen on a microscope slide about one-half its volume of a saturated aqueous or absolute alcoholic solution of picric acid, the spermatic liquid gradually becomes turbid owing to the separation of small, yellow, rhombic needles from 5 to 20 μ , or even greater, in length. If a spot on clothing is to be examined for the presence of semen, the spot is extracted in the ordinary way with a little water and the solution then tested with picric acid. If the picric acid is added in excess or if the solution is too dilute, the reaction loses in distinctness, so that it is best to add a platinum wire loopful of the saturated solution at first, further additions being made in case of necessity. The presence of blood, if not in large amount, does not interfere with the reaction. Microscopic examination shows that the crystals are strongly refractile and that they are often traversed by a longitudinal, refractile line. The obtuse angles are generally, and the acute ones sometimes, rounded. The crystals are sometimes twinned, usually in the form of a cross, and also form drusy aggregates. The reaction is extremely sensitive and takes place in both alkaline and acid solutions, provided that the acidity or alkalinity is not excessive. Semen dried on linen is capable of supporting a temperature of 150° for an hour without causing failure of the reaction, which will, however, not take place if a temperature of 200° is maintained for a few minutes.

The chemical nature of the crystals has not yet been ascertained. The only substance found by the author to give with picric acid crystals at all resembling those obtained with semen is Poehl's spermine, but with this compound the reaction does not succeed after heating at 100° for half an hour.

Experiments are to be made with the semen of animals to decide whether the reaction is peculiar to human semen or otherwise.

T. H. P.

General and Physical Chemistry.

Absorption and Emission Lines of Gaseous Substances. HENDRIK A. LORENTZ (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 591—611).—Almost entirely mathematical. The author suggests a mechanism by which the regular vibrations of light may be transformed into an unordered motion that may be called heat. So long as the molecule of a gas does not collide with another molecule, the movable electron within it may be regarded as free to follow the periodic electric forces of the light beam, and it will accordingly move with an amplitude which would continually increase if the frequency of the incident light corresponded exactly to that of the free vibrations of the electron. The collisions of the molecules, however, will prevent the amplitude of the vibrations from exceeding a certain limit. The formulæ deduced by the author make it possible to calculate N , the number of molecules per unit volume, and T , the mean length of time during which the vibration in a molecule is left undisturbed. Thus for the absorption of the dark heat rays by carbon dioxide, $N = 6 \times 10^{17}$ and $T = 10^{-14}$ sec.; for the absorption in a sodium flame, $N = 4 \times 10^{14}$ and T lies between 12×10^{-12} and 24×10^{12} sec. J. C. P.

Relationship between the Molecular Weight and the Rotation of an Active Compound in Solution. PAUL WALDEN (*Ber.*, 1906, 39, 658—676. Compare Abstr., 1905, ii, 130).—A reply to Patterson's criticisms (this vol., ii, 61). The data of the molecular weight determinations are given in detail, and the concentrations are not regarded as being so high as to invalidate the conclusions previously drawn. In the majority of cases, the molecular weight diminishes as the concentration increases (compare Beckmann, Abstr., 1891, 437). It is maintained that there is a certain relationship between the rotation and molecular weight in various solvents, and this is shown by the arrangement of the data in several tables. When the values are calculated for infinite dilution by extrapolation for benzene, ethyl acetate, methyl alcohol, acetone, and chloroform solutions of some five active esters, the following statements are found to hold good. (1) The values for M approximate to the theoretical most nearly in benzene solutions, and the order of arrangement according to increasing values of M is the same for all five active compounds, namely, benzene \rightarrow ethyl acetate \rightarrow methyl alcohol \rightarrow acetone. (2) The rotation values may be arranged in the same order, and an increase in the rotation thus corresponds with a rise in the molecular weight. An exception is met with in methyl acetylmalate. The relationship is of a qualitative nature only. J. J. S.

Influence of Temperature and Concentration on the Specific Rotation of Optically Active Substances. HERMANN GROSSMANN and LEO WIENEKE (*Zeit. physikal. Chem.*, 1906, 54, 385—427).—Over the temperature and concentration ranges (10 — 90° and 11 — 38

per cent. respectively) covered by the authors' work, the specific rotation of tartaric acid increases with rising temperature and falling concentration (compare Thomsen, Abstr., 1886, 12; Přibram and Glucksmann, Abstr., 1898, ii, 321, 494; Wendell, Abstr., 1899, ii, 199; Winther, Abstr., 1902, ii, 589). The specific rotation of sodium hydrogen tartrate decreases slightly with falling concentration, but increases with rising temperature up to about 50° , after which there is a decrease (compare Grossmann and Pötter, Abstr., 1904, ii, 153). A 25 per cent. solution of sodium potassium tartrate has a specific rotation which increases slightly with rising temperature up to 30° , whilst from 30° to 90° it is practically constant (compare Winther, *loc. cit.*).

Addition of boric acid to solutions of tartaric acid markedly increases the rotation of the latter. The authors have prepared, as far as possible, $2N$, N , $N/2$, $N/4$, $N/8$ solutions containing tartaric and boric acids in the molecular proportions 3 : 1, 2 : 1, 1 : 1, 1 : 2, and 1 : 3 respectively, and determined the rotation of these solutions at temperatures between 10° and 90° . The general character of the influence of temperature and concentration on the molecular rotation of tartaric acid in these solutions may be seen from the following numbers, which apply to the molecular combination $3C_4H_6O_4 + 1H_3BO_3$:

Concentration.	$[M]_D$ at 10° .	$[M]_D$ at 90° .
$2N$	58.4°	49.6°
N	54.4	41.4
$N/2$	49.4	38.2
$N/4$	42.4	35.4
$N/8$	38.1	31.2

$[M]_D$ at 10° for tartaric acid ($N/4$ solution) mixed with boric acid in the five molecular proportions mentioned above is found to be 42.4° , 49.2° , 59.5° , 71.4° , and 78.1° respectively. The results point to the existence in solution of a boryl tartrate (compare Magnanini, Abstr., 1890, 1357; Hädrich, Abstr., 1894, ii, 78), a conclusion supported also by the study of the change in the rotation of sodium hydrogen tartrate produced by boric acid. The magnitude of this change, as dependent on temperature and concentration, is generally similar to that observed in the case of tartaric and boric acids. The authors' experiments make probable also the existence of a sodium boryl ditartrate, especially in the more concentrated solutions.

The molecular rotation of potassium antimonyl tartrate in aqueous solution is practically independent of the concentration at the ordinary temperature. As the temperature rises, the molecular rotation decreases slightly, probably owing to hydrolysis, and the decrease is more marked in the more dilute solutions.

The molecular rotation of tartaric acid in presence of a molecular quantity of pyridine is approximately the same as that of alkali hydrogen tartrates, and diminishes slightly as the dilution increases. A slight regular decrease of the rotation follows also on a rise of temperature, except for $N/4$ and $N/8$ solutions, in which cases there is an ill-defined maximum of $[M]_D$ about 40 — 60° . When two mole-

cules of pyridine are taken for one molecule of tartaric acid, there is a regular decrease of the molecular rotation both with rising temperature and diminishing concentration. The authors' experiments point to the existence of an acid and a normal pyridine tartrate.

The specific rotation of a $2N$ solution of malic acid is found to be $+0.1^\circ$ at 10° , but rising temperature and increasing dilution both have the effect of making the rotation negative. Thus at 90° the specific rotation of the $2N$ solution is -3.8° , whilst at 20° the values of $[\alpha]_D$ for $2N$, N , $0.5N$, $0.25N$, and $0.125N$ solutions are -0.5° , -1.1° , -2.1° , -3.0° , and -3.6° respectively. The specific rotation (negative) of ammonium hydrogen malate does not vary much with the concentration, but falls off as the temperature rises.

The behaviour of solutions of malic and boric acids in different molecular proportions has been studied. Boric acid increases the negative rotation of malic acid, and the existence of a boryl malate is probable, but not definitely established. When ammonium hydrogen malate is mixed with the equivalent quantity of boric acid, the negative rotation of the former is increased, and the existence of a complex ammonium boryl malate is probable. For a normal solution there is a regular increase of the specific rotation with rising temperature, for a $N/2$ solution there is a maximum of the rotation at 60° , and for a $N/4$ solution there is a maximum at 40° .

The presence of pyridine increases the negative rotation of malic acid. Thus, at 10° , for N malic acid $[\alpha]_D - 0.7^\circ$, for N malic acid containing a molecular quantity of pyridine $[\alpha]_D - 9.7^\circ$, for N malic acid containing twice the molecular quantity of pyridine $[\alpha]_D - 12.2^\circ$. The negative rotation falls off in both the latter cases with diminishing concentration and rising temperature. The results point to the formation of acid and normal malates of pyridine.

J. C. P.

Influence of Concentration and Temperature on the Specific Rotatory Power of Strongly Optically Active Compounds. II. HERMANN GROSSMANN and HEINZ PÖTTER (*Ber.*, 1905, **38**, 3874—3891. Compare Grossmann and Wieneke, preceding abstract).—The boryl tartrates are dissociated by dilution and rise of temperature, giving lower values for the rotatory power. In the present paper, the investigation is extended to the molybdates and tungstates, somewhat more complex results being obtained. Thus dilution decreases the rotatory power of sodium molybdyd tartrate, $\text{Na}_2\text{MoO}_4 + \text{C}_4\text{H}_4\text{O}_6 = \text{Na}_2(\text{MoO}_3)_2\text{C}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$, very strongly and less strongly that of potassium molybdyd ditartrate, $\text{MoO}_2(\text{C}_4\text{H}_4\text{O}_6\text{K})_2$, but increases that of the corresponding sodium tungstyl tartrate, $\text{WO}_2(\text{C}_4\text{H}_4\text{O}_6\text{Na})_2$; in the latter case, however, the curve indicates that a maximum rotation would soon be reached.

With rise of temperature, the rotatory power of sodium molybdyd tartrate falls rapidly, whilst that of sodium tungstyl ditartrate exhibits a very pronounced maximum at 40° .

T. M. L.

Radioactivity of Springs of Potable Waters. F. DIENERT and E. BOUQUET (*Compt. rend.*, 1906, **142**, 449—450).—Using Elster and Geitel's electroscope, the authors have examined the waters of four

springs which feed the river Avre, and find that they are all radioactive, the activity, as measured by the intensity of the current of discharge of the electroscope by the emanation evolved by 1 litre of the water, varying from 1.40×10^{-13} to 2.55×10^{-13} ampere. The air in the chamber in which the water is collected is also radioactive, and the most radioactive of the waters is most free from *Bacillus coli communis*.
M. A. W.

Properties of the α -Rays Emitted by Radium and by Substances rendered Active by Radium Emanation. HENRI BECQUEREL (*Compt. rend.*, 1906, 142, 365—371. Compare Abstr., 1903, ii, 256, 523).—The source of the α -rays, of linear form, was placed at a distance of 2.145 cm. from a parallel slit, on the other side of which was a photographic plate at a distance of 1.94 cm., the whole being placed in a strong magnetic field. One half of the beam of rays was made to pass through a sheet of aluminium 0.015 mm. thick, whilst the entire path of the other half was through air. The deviation of the former was found to be about 10 per cent. greater than that of the latter when the intensity of the field was about 9600 units. This result corresponds with a greater diminution of the velocity of the α -particles after passing through the layer of aluminium.

Further experiments were made to determine the trajectory of the particles through air. The beam of α -rays emitted by a thin platinum wire previously exposed to radium emanation after passing through a parallel slit was received on an inclined photographic plate normal to the non-deviated rays. Impressions were taken when the platinum wire was covered with a thin sheet of aluminium and when uncovered, and on account of the decreasing activity of the radiating source the magnetic field was reversed every five minutes. Two divergent curves were thus obtained, from which the form of the trajectory of the particles has been deduced. Within the limits of the experiments, the radius of curvature of the trajectory is practically constant; the variation is at any rate smaller than the experimental errors. The comparison of the curves for rays which had traversed a very thin layer of aluminium with those for rays which had only passed through air leads to the same conclusion as the previous experiments.

H. M. D.

β -Polonium. FRIEDRICH GIESEL (*Ber.*, 1906, 39, 780—782).—The name β -polonium is given to the radioactive constituent of bismuth oxychloride prepared from barium-lead-radium sulphate obtained from pitchblende; it emits β -rays and thus differs from Madame Curie's "polonium." The radioactivity decreases to half its value in 6.14 days, the constant of decay being 0.1128; the life of the atom of β -polonium is thus 8.86 days.

W. A. D.

The Carbon Cell. FRITZ HABER and LUDWIK BRUNER (*Zeit. Elektrochem.*, 1906, 12, 78—79).—In a former memoir on this subject (Abstr., 1904, ii, 626), the authors calculated the *E.M.F.* of the hydrogen-oxygen cell at high temperatures by means of Bose's determinations of the *E.M.F.* at low temperatures, and Helmholtz's formula integrated

by means of an expression for the temperature-coefficient of the heat of formation of steam based on Mallard and Le Chatelier's values of the specific heats. It appears that these data are inaccurate, and a new calculation is made based on the measurements of the dissociation of steam made by Nernst and Wartenberg, and Langen's determinations of the specific heats of hydrogen, oxygen, and steam. The values thus obtained are compatible with the assumption that the vapour-pressure of steam in equilibrium with fused sodium hydroxide is approximately equal to that in ordinary moist air. T. E.

Filaments for Incandescent Electric Lamps. SIEMENS & HALSKE, AKTIEN-GESELLSCHAFT (D.R.-P. 161081).—The filaments are composed of an intimate mixture of metallic tantalum with an electrolytically conducting oxide, such as zirconia. Unlike filaments of oxides alone, they may be used in exhausted vessels, thus economising energy. They may be prepared by mixing the metal and oxide with paraffin and igniting, or by making an intimate mixture of the conducting oxide with tantalum oxide and heating electrically in a vacuum, the oxygen being pumped off as produced. C. H. D.

The Anodic Attack of Iron by Stray Currents in the Earth and the Passivity of Iron. FRITZ HABER and F. GOLDSCHMIDT (*Zeit. Elektrochem.*, 1906, 12, 49—74).—In electric tramways, the rails are usually connected to the negative terminal of the central generators; the stray earth currents therefore flow from the rails through the earth (or iron pipes) towards the central power station. The difference of potential between two points in the earth may be measured by means of unpolarisable electrodes of zinc immersed in a paste of zinc sulphate crystals, which are placed in holes in the earth at suitable distances apart. A non-polarisable coulomb-meter, by means of which earth currents may be measured, is also described.

Cast-iron, when buried underground, is sometimes acted on in such a way that its appearance is not much changed, but the metal is removed, leaving a soft, porous mass of ferrous phosphate and silicate mixed with particles of iron and carbon. The action may take place independently of electric currents. Owing to the high resistance of the earth, stray currents can be rarely large enough to produce rapid deterioration of iron pipes; in cases where, owing to high local conductivity of the earth, a considerable current might be concentrated on a small area of iron, the effect will depend mainly on whether the iron is active or passive. The anodic behaviour of iron in solutions of normal carbonates, hydrogen carbonates, hydroxides, and chlorides is therefore studied. An iron anode is attacked rapidly in a solution of carbon dioxide or of a hydrogen carbonate. In solutions of normal alkali carbonates, an iron anode is passive so long as circulation is kept up, but if it is stopped or diminished by means of a diaphragm, hydrogen carbonate is formed at the anode, and the attack begins. Measurements of the potential of the iron allow its behaviour to be followed readily, since there is a difference of potential between active and passive iron of considerably more than 1 volt. In this way it is shown that an iron anode is active in a very dilute solution of sodium carbonate and passive in

concentrated solutions, whilst in a 1/20 *N*-solution the same anode may be partially active and partially passive. The conditions under which this state of things can exist are, however, not easily maintained, and, as a rule, the active or the passive state soon gains the upper hand, the whole anode passing into the one or other condition. An iron anode which is passive in a solution of sodium or calcium hydroxide is at once rendered active by the addition of a chloride.

The authors discuss the cause of passivity very fully. They take the view that a skin of oxide is formed which is a metallic conductor. The oxide Fe_3O_{11} is shown to possess metallic conductivity. In order to explain the loss of passivity which a passive anode undergoes when left without current, it is assumed that the skin of oxide becomes discontinuous or porous. The behaviour of a metal covered by a porous skin of a less readily attacked substance is studied on iron coated with copper and on thin platinum or silver foil coated on one side with zinc. In the first case, as the thickness of the copper deposit is increased the electrical behaviour of the coated iron changes gradually from that of iron to that of copper. In the second case, a drop of a solution of zinc sulphate is placed on the platinum or silver foil on the uncoated side, and the potential difference between the metal and the solution measured. It is found to approach more and more nearly to that between zinc and a solution of zinc sulphate as the porosity of the platinum or silver foil increases. The skin of oxide supposed to exist on the surface of a passive iron anode differs from the porous metallic films in the fact that its imperfections are immediately remedied by the oxidation of the metal. Capillary forces and reduction of the oxide by the metal with which it is in contact are suggested as reasons for the formation of defects in the skin, which is thus supposed to be constantly undergoing destruction and regeneration.

T. E.

Electro-deposition of Copper on Iron. OLIVER W. BROWN and FRANK C. MATHERS (*J. Physical Chem.*, 1906, 10, 39—51).—The author has endeavoured to find a bath suitable for deposition of copper on iron, which shall not contain cyanide. The best bath is made as follows: 60 grams of copper sulphate, 50 grams of sodium hydroxide, 159 grams of sodium potassium tartrate, and 1000 c.c. of water; the best working conditions being a cathode density of from 0.1 to 0.5 ampere per square decimetre and an anode density not exceeding 1.04 amperes per square decimetre. This bath is preferable to cyanide baths, as it gives off no offensive gas, works at a higher anode density, and requires a lower voltage.

L. M. J.

Electrolysis with Alternating Currents. I. Electrolysis of Alkali Chlorides. ANGELO COPPADORO (*Gazzetta*, 1905, 35, ii, 604—628).—On passing a current of 42 alternations per second through an aqueous solution of sodium or potassium chloride of about 3-*N* concentration, the electrodes being of platinum and the temperature between 15° and 30°, no decomposition of the electrolyte occurs until the current density reaches the value 50 amperes per sq. cm. With current densities higher than this, an appreciable amount of

hypochlorite is formed. The gas evolved consists of hydrogen, oxygen being also set free after the electrolysis has continued for some time; chlorine is only evolved in traces and at the beginning of the action. In no case was the formation of chlorate observed. The electrodes undergo disintegration and partly dissolve in the electrolyte; a deposit forms on the bottom of the cell, consisting, with potassium chloride, of platinum black mixed with potassium platinichloride, and in the case of sodium chloride of platinum black alone. If the current density is not too high, the electrodes become platinised, and when this action is complete no more gas is evolved or hypochlorite formed. The hypochlorite is afterwards decomposed into chlorine and oxygen by the catalytic action of the finely-divided platinum suspended in the liquid. Owing to the platinising of the electrodes, which diminishes the polarisation, the difference of potential at the electrodes falls appreciably as the electrolysis proceeds. With graphite electrodes, a current density of more than 1000 amperes per sq. cm. is necessary before appreciable formation of hypochlorite occurs; the electrodes then undergo very considerable disintegration. T. H. P.

Electrolytic Researches with Symmetrical and Unsymmetrical Alternating Currents. ALBERT LÖB (*Zeit. Elektrochem.*, 1906, 12, 79—90).—The author has continued the experiments of Le Blanc and Schick (*Abstr.*, 1904, ii, 229, and this vol., ii, 5). Using copper electrodes, a solution of potassium cyanide, and an alternating current, the quantity of copper dissolved in similar circumstances depends on the nature of the surface of the electrodes. The smoother the surface, the smaller is the quantity dissolved. The same behaviour is observed with zinc and nickel electrodes in cyanide solutions. In all cases, the loss of weight of the electrodes is increased by raising the current density, by increasing the concentration of the potassium cyanide, and by diminishing the number of alternations per minute. Iron and nickel are exceptional in the particular that they become passive at high current densities, and therefore their solubilities become less.

With lead electrodes in 4*N*-sulphuric acid, a current density of 0.04 to 0.1 ampere per sq. cm., and about 3000 alternations per minute, lead sulphate is formed and hydrogen evolved, the yield of lead sulphate being about 60 per cent. of the theoretical amount; with increasing frequency the yield diminishes, becoming almost zero at 17,000 alternations per minute; the yield also falls off when the frequency is diminished. These facts are explained by supposing that in 1/17,000 minute the formation of solid lead sulphate from the lead ions produced by one current impulse has practically not begun, hence the lead ions are reconverted into metallic lead by the next opposite impulse; at low frequencies, on the other hand, the duration of an impulse is sufficient to produce lead sulphate in such quantity that it adheres to the electrode and diminishes its active surface so that the potential can rise to that required for the oxidation of the lead sulphate to lead peroxide.

Increasing frequency also diminishes the yield of zinc oxalate obtained from zinc electrodes in oxalic acid.

With direct current, copper usually dissolves in potassium cyanide in the cuprous state, but the quantity dissolved is often less than that required by Faraday's law; the two lowest values observed were 37.1 and 44.5 per cent. of the theoretical quantity. The reason of this apparent passivity was not discovered.

Some experiments with unsymmetrical alternating currents were made with copper and lead electrodes in solutions of potassium cyanide and sulphuric acid respectively. They are in agreement with the results obtained with the symmetrical current. T. E.

Electrolytic Reduction of Succinimide. JULIUS TAFEL and BRUNO EMMERT (*Zeit. physikal. Chem.*, 1906, **54**, 433—450).—The earlier work on this subject (Tafel and Naumann, *Abstr.*, 1905, ii, 224) has been continued. The electrolytic reduction of succinimide is in several respects a more complicated process than the corresponding reduction of caffeine (*loc. cit.*). Lead, particularly in spongy form, exerts a specially favourable influence on the reduction of succinimide. Further, the "acid potential" (that is, the potential at the cathode during the electrolysis of pure acid of various concentrations) at a lead cathode is markedly raised both by succinimide and by pyrrolidone, the product of its reduction. The reducing efficiency of a lead cathode remains practically constant throughout one experiment in the case of caffeine, whilst it rises gradually in the case of succinimide, probably owing to modification of the surface of the lead cathode and the increase of catalytic action resulting therefrom. The efficiency of a lead cathode in the reduction of succinimide rises with increasing acid concentration up to 60 per cent., subsequently falling off. With caffeine, on the other hand, the reducing efficiency of a lead cathode is constant for acid of 10—30 per cent. concentration, and falls off as the acid concentration increases. J. C. P.

Elimination of Thermometer Lag in Calorimetry. WILHELM JAEGER and HELMUTH VON STEINWEHR (*Zeit. physikal. Chem.*, 1906, **54**, 428—432).—The sources of error dealt with by Richards, Henderson, and Forbes (*Abstr.*, 1905, ii, 677) had been discussed previously by the authors (*Verh. deut. physikal. Ges.*, 1903, **5**, 50, 353; see also *Abstr.*, 1905, ii, 677). It is thought, in view of the many other sources of error associated with the mercury thermometer, that too much relative importance has been attached to thermometer lag by Richards, Henderson, and Forbes. Platinum thermometers are again recommended in preference to mercury thermometers for calorimetric work. J. C. P.

Molecular Attraction. V. An Application of the Theory to Ten Additional Substances. JAMES E. MILLS (*J. Physical Chem.*, 1906, **10**, 1—38).—An extension of the author's previous paper (*Abstr.*, 1904, ii, 642), the additional substances investigated being methyl formate, ethyl formate, methyl acetate, chloroform, acetone, carbon disulphide, ammonia, carbon dioxide, nitrous oxide, and sulphur dioxide. Of these, seven are in accord with the theory, the value $(L - E) / \sqrt[3]{d - \sqrt[3]{D}}$ remaining constant. Three substances, carbon

dioxide, nitrous oxide, and sulphur dioxide, showed considerable divergence, but this can probably be attributed wholly to errors in the measurements employed. The values of the heat of vaporisation are recalculated by the author's formula as well as by Crompton's equation, and it is found that the latter gives values in good accord with the results at high temperatures, but that at low temperatures the results are too high. The author's expression gives results in accord over the whole range of temperature. With the exception of values near the critical temperature, out of 378 tests now applied by the author only 29 show a divergence greater than 2 per cent., and only three greater than 5 per cent.

L. M. J.

Boiling Points of Saturated Solutions in Binary Systems in which a Compound occurs. H. W. BAKHUIS ROOZEBOOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 536—541).—A theoretical paper. The author deals with the boiling phenomena as these are affected by the different volatility of the two constituents. It seems probable that a saturated solution of the kind described in the title may have two boiling points.

J. C. P.

Recombination of the Ions of Salt Vapours. GEORGES MOREAU (*Compt. rend.*, 1906, 142, 392—394. Compare Abstr., 1904, ii, 536).—A current of air was passed through a salt solution of known concentration, then through a porcelain tube heated to redness, and finally through a brass tube. The concentration of the ions in the brass tube was determined by measuring the saturation current between the tube and two small concentric cylindrical electrodes placed close together along the axis of the tube. Solutions of potassium chloride, bromide, iodide, nitrate, and carbonate and of rubidium chloride of different concentrations were used, and the distance of the electrode pair from the hot tube was varied. The experimental data show that at a given temperature the rate of recombination of the ions is inversely proportional to the square root of the concentration of the salt vapour, and that the rate increases with increasing temperature. By means of Langevin's formula, the ratio of the number of combinations to the number of collisions between ions of the same mobility is calculated. At 80°, this ratio is equal to 0.61, at 15° it is very nearly equal to unity. The high value of the ratio agrees with the author's view that the changed ions are complex in character, and that this complexity increases with falling temperature.

H. M. D.

Connection between Viscosity and Ionic Velocity or Rate of Diffusion. PAUL WALDEN (*Zeit. Elektrochem.*, 1906, 12, 77—78).—For solutions of chlorine, bromine, and iodine in different solvents it is shown that the product of the diffusion constant, D , and the viscosity, η , of the solvent is independent of the nature of the solvent. If this product is multiplied by the square root of the molecular weight, M , of the halogen, a number is obtained which is independent of the nature of the halogen, or in symbols $D\eta \cdot \sqrt{M} = 0.146$. The value of this constant is also independent of the temperature.

T. E.

Viscosity and Fluidity. EUGENE C. BINGHAM (*Amer. Chem. J.*, 1906, **35**, 195—217. Compare Jones and Bingham, this vol., ii, 66).—Theoretical considerations are advanced which indicate that fluidities are additive and that the normal viscosity curve of simple mixtures is hyperbolic. The viscosity data of Linebarger (*Amer. J. Sci.*, 1896, **2**, 331), Thorpe and Rodger (*Trans.*, 1897, **71**, 374), and Dunstan (*Trans.*, 1904, **85**, 819) are quoted and plotted as curves, and it is shown that, in general, the fluidity curves of simple mixtures are nearly straight lines. Explanations are offered for cases in which the fluidity curve apparently deviates from a straight line. It is pointed out that there appears to be a relation between changes in fluidity and other physical properties.

In the case of pure liquids, it has been found that the fluidity curves are very nearly straight lines for all non-associated compounds, and that the fluidities of the compounds in a homologous series at any given temperature decrease regularly as the molecular weight increases.

E. G.

Existence of Hydrogen Carbonates in Mineral Waters and the Supposed Anomalies in the Osmotic Pressure Values. LOUIS C. MAILLARD and LUCIEN GRAUX (*Compt. rend.*, 1906, **142**, 404—407).—The authors find that the freezing point of a mineral water from Chatel-Guyon, when calculated from its chemical composition on the assumption that the carbonic acid is present in the form of hydrogen carbonates and that the various electrolytes are completely dissociated, is -0.388° , the actual freezing point being -0.338° . The opinion previously expressed that hydrogen carbonates cannot be present in such mineral waters is retracted. H. M. D.

Significance of the Discontinuity of dP/dT in the Application of the Phase Rule. NICOLAI N. SCHILLER (*Zeit. physikal. Chem.*, 1906, **54**, 451—454).—A theoretical paper. J. C. P.

An Apparent Case of Chemical Action at a Distance. RAPHAEL E. LIESEGANG (*Ann. Physik*, 1906, [iv], **19**, 395—406).—If two drops of silver nitrate are placed on a gelatin film containing potassium bromide, it is observed that the masses of silver bromide produced by diffusion frequently grow more rapidly on the sides of the two drops which face each other. This apparent attraction is attributed to the gelatin becoming poorer in potassium bromide in the neighbourhood of the nascent silver bromide. This poverty of potassium bromide will be more marked on the line joining the two drops, and will permit a more rapid growth of the silver bromide masses in that direction. J. C. P.

Colorimetric Measurement of Affinity. EDUARD SALM (*Zeit. Elektrochem.*, 1906, **12**, 99—101).—The concentration of the hydrogen ions in any solution may be determined by adding a suitable indicator to the solution and comparing the colour with that of one of the standard solutions of known hydrogen ion concentration (*Abstr.*, 1904, ii, 536) containing the same indicator. In this way the dissociation constant of an acid may be readily determined. The following

values are obtained in this way (the figures in brackets are calculated from Ostwald's measurements of electrolytic conductivity): oxalic acid, $K=0.09$ (0.1); tartaric acid, $K=0.0011$ (0.00097); fumaric acid, $K=0.0011$ (0.00093); camphoric acid, $K=0.000025$ (0.0000225).

The dissociation constant K of an indicator is easily determined. For a binary acid it follows from Ostwald's law of dilution that $K=C_{H^+}$, where C_{H^+} is the concentration of the hydrogen ions when one half of the electrolyte is dissociated. This concentration is found for litmus, for example, by adding an acid to a solution of litmus until the colour is the same as that obtained by superposing equal depths of solutions of blue and red litmus. An alkaline solution of phenolphthalein is acidified until its colour is equal to that of a layer of the alkaline solution of one-half the depth. The concentration of the hydrogen ions in these half dissociated solutions is then determined by means of concentration cells with hydrogen electrodes. The following results are given: methyl-orange, $K=4.6 \times 10^{-4}$; *p*-nitrophenol, $K=2.3 \times 10^{-7}$; rosolic acid, $K=1.1 \times 10^{-8}$; alizarin, $K=8.8 \times 10^{-9}$; phenolphthalein, $K=8 \times 10^{-10}$; cyanin, $K=4.2 \times 10^{-6}$; dimethyl-aminoazobenzene, $K=1.45 \times 10^{-11}$. T. E.

Chemical Equilibrium between Silver Amalgams and a Solution of Silver and Mercury Nitrates. WILLEM REINDERS (*Zeit. physikal. Chem.*, 1906, 54, 609—627. Compare Abstr., 1902, ii, 639; also Ogg, Abstr., 1899, ii, 14).—Measured quantities of solutions of silver nitrate and mercurous nitrate were mixed and put into a tube along with a weighed quantity of metal. The tube was then sealed, and shaken in a thermostat at 25° for a considerable time (ten to thirty days). The tube was then opened, the potential difference of the metallic residue against the solution was determined, and an analysis was made both of the metallic residue and of the solution.

Silver and mercury form several compounds, namely, Ag_3Hg_4 , Ag_3Hg_2 , and probably Ag_3Hg . It is found that liquid amalgams containing 0—0.076 per cent. Ag coexist with solutions in which the silver nitrate is 0—2.5 per cent. of the total salts; the compound Ag_3Hg_4 coexists with solutions containing from 2.5 to 18 per cent. of silver nitrate; the compound Ag_3Hg_2 coexists with solutions containing from 18 to 40 per cent. of silver nitrate; the compound Ag_3Hg coexists with solutions containing from 40 to 100 (nearly) per cent. of silver nitrate; solid solutions of mercury in silver coexist with solutions containing practically nothing but silver nitrate. The potential difference metal/solution changes with composition in a manner which is in harmony with the equilibria just described and with the author's earlier theoretical work (*loc. cit.*). J. C. P.

Ester Formation. HEINRICH GOLDSCHMIDT and EINAR SUNDE (*Ber.*, 1906, 39, 711—725).—The velocities of esterification of various organic acids with ethyl alcohol in the presence of a catalyst were measured. The ethyl alcohol used was found, after the measurements had been made, to have been not quite anhydrous, since it had been dried over quicklime only. Phenylacetic acid in varying dilutions with ethyl alcohol was esterified with hydrogen chloride as the catalyst.

Measurements of the velocity of esterification of acetic, trichloroacetic, and dichloroacetic acids respectively were made similarly. Phenylacetic acid and acetic acid were esterified by the use of picric acid or trichloroacetic acid as the catalyst. Acetic acid was esterified by the use of dichloroacetic acid as the catalyst. A mixture of picric acid and aniline picrate was used as the catalyst during the esterification of phenylacetic acid and acetic acid, whilst a mixture of trichloroacetic acid and aniline trichloroacetate was used for the esterification of acetic acid. The temperature was maintained at 25° in all the experiments.

Ester formation, at least under the conditions examined by the authors, is fundamentally a reaction of the first order, although the values for the esterification constant in any one set of experiments fall as the reaction proceeds. The latter effect is due to the retarding influence of the water formed.

The acceleration of esterification varies according to the catalyst used. The results indicate a connection between the degree of dissociation of the acids used as catalyst and the esterification constants.

The results obtained are discussed at length.

A. McK.

Catalysis by Ferments. GEORGE SENTER (*Zeit. physiol. Chem.*, 1906, 47, 126—128).—Mainly polemical. Criticisms are offered on Euler's work (*Abstr.*, 1905, ii, 693). The author adheres to his earlier opinion that catalysis by catalases is a heterogeneous reaction, the velocity of which is influenced by diffusion.

W. D. H.

Reciprocal Behaviour of Solute and Solvent. NICOLAI N. SCHILLER (*Zeit. physikal. Chem.*, 1906, 54, 455—462).—A mathematical paper.

J. C. P.

Crystalline Habit. F. G. COTTRELL (*J. Physical Chem.*, 1906, 10, 52—57).—The author briefly discusses the factors which determine the crystalline habit. According to the views of Gibbs, who treats the question as one of equilibrium, those faces are developed by the crystal in greatest extent which have, in contact with the solution, the lowest surface tension. The author finds that an octahedral crystal of salt, produced from a solution containing 10 per cent. of urea, in the course of a day developed truncated corners to a very slight extent when placed in a saturated solution of salt in water, but no further development took place in two months. The author considers therefore that explanation for crystal habit is to be sought not in equations defining equilibrium, but in terms defining rate of growth which disappear in the final equations of equilibrium.

L. M. J.

Nature of "Liquid Crystals." III. GUSTAV TAMMANN (*Ann. Physik*, 1906, [iv], 19, 421—425).—The author suggests that the behaviour of a substance forming so-called "liquid crystals" is very similar to the behaviour which would be exhibited by a compound A_mB_n , forming a continuous series of mixed crystals with its components A and B, which on melting dissociated largely into its components, these not being miscible in all proportions.

J. C. P.

Simple Arrangement of Lenses for Reading the Graduations of Chemical and Assay Balances. GEORGE T. HOLLOWAY (*Analyst*, 1906, 31, 39.)—A 3-inch plano-convex lens cemented with seccotine to the inside of the glass front of the balance opposite the pointer scale will be found to be very convenient. A 2-inch lens similarly fixed opposite the beam graduations is also useful. The focal length of the lenses is of little importance, but they must not be powerful enough to produce distortion. W. P. S.

Non-leaking Glass Tap. A. P. CHATTOCK (*Phil. Mag.*, 1906, [vi], 11, 379—380).—The two tubes which are connected through the tap are sealed to the same side of the latter. The plug of the tap is hollow, contains mercury, and has two holes corresponding with the ends of the tubes. When the tubes are to be disconnected, the plug is turned so that its two holes are below the mercury. If a leak occurs, gas may get into the plug, but no farther. J. C. P.

Carburetted Water Gas in the Bunsen Burner. MASUMI CHIKASHIGE (*J. Soc. Chem. Ind.*, 1906, 25, 155—156. Compare *Abstr.*, 1904, ii, 254.)—Carburetted water gas suitable for laboratory purposes is produced by injecting heavy petroleum oils, together with steam, into a water-gas generator filled with ignited coke; the gas produced is passed through a superheater loosely packed with fire-bricks, and then through a scrubber, after which it enters the gas-holders. The mean composition of the gas does not differ much from that of coal gas. Heavy hydrocarbons 5.3, methane 16.8, hydrogen 51.7, carbon monoxide 15.4, carbon dioxide 0.6, oxygen 0.5, nitrogen 9.7 per cent. by volume. The gas was tested with Smithells and Ingle's apparatus to find out the proportions of the constituents of the partially burned gas, and the results are tabulated. The flow of gas necessary to produce a flame 15 cm. long from a Bunsen burner was found to be 160 litres per hour as compared with 120 litres per hour for coal gas. Carburetted gas has no more action on copper, platinum, or porcelain vessels than coal gas has. P. H.

Inorganic Chemistry.

Oxyhalogen Compounds. I and II. WILLIAM BRAY (*Zeit. physikal. Chem.*, 1906, **54**, 463—497).—The author first discusses the kinds of experimental evidence that may help in deciding the question whether any given reaction takes place in stages, and, if so, what these stages are. The evidence may be classified under four heads: (1) isolation of an intermediate product; (2) the occurrence of coupled processes (see Luther and Schiloff, *Abstr.*, 1904, ii, 244); (3) kinetic experiments by which the order of the reaction is determined; (4) analogy.

In the experimental part of the work, the oxidation of iodide by potassium permanganate, hypochlorous acid, and ozone has been studied, and the results confirm the view expressed by Förster and Gyr (Abstr., 1903, ii, 209), that the production of iodate in the oxidation of an iodide is a secondary process. Förster and Gyr concluded that the production of iodine was the primary process, but the author shows that the formation of hypoiodite may just as well be regarded as the primary stage. On the basis of work due to various authors, it can be shown that when an iodide is oxidised by hydrogen peroxide, potassium persulphate, arsenic acid, and iodic acid, the primary formation of hypoiodite is practically certain, and a similar explanation is at least in harmony with recorded observations on the oxidation of iodide by bromic, chloric, and chromic acids. The author, therefore, feels justified in formulating the rule that when an iodide is oxidised by substances containing oxygen, the first stage is the production of hypoiodite or hypoiodous acid (compare Skrabal, Abstr., 1905, ii, 449). It is very probable also that a similar rule will apply to the oxidation of chloride and bromide, and that in an aqueous solution of a halogen X the active constituent is an acid of the type HXO .

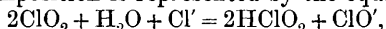
The normal oxidation potential of the process $IO_3' \rightarrow I$ is higher than that of the process $HIO \rightarrow I$.

Incidentally it has been shown that iodine can be estimated by thiosulphate in sodium hydrogen carbonate solution, provided the solution is saturated with carbon dioxide and contains enough iodide (about 0.1 mol. per litre).
J. C. P.

Oxyhalogen Compounds. III. Chlorine Peroxide. WILLIAM BRAY (*Zeit. physikal. Chem.*, 1906, **54**, 569—608. Compare preceding abstract).—The ratio in which chlorine peroxide is distributed between water and carbon tetrachloride is nearly independent of the concentration, hence the molecular condition of the peroxide is the same in both solvents. Cryoscopic experiments with the aqueous solutions show that the formula of the dissolved peroxide is ClO_2 . The eutectic point at which ice, chlorine peroxide hydrate, and solution are in equilibrium is -0.79° . The solubilities of the hydrate and of the liquid peroxide have been determined at various temperatures up to 15° , and the curves obtained show that at 18° there is a transition point, the hydrate being there converted into the liquid peroxide. Chlorine peroxide hydrate is a rather unstable substance and its composition could not be determined with any very great accuracy. The author considers it to be $ClO_2 \cdot 8H_2O (\pm 1H_2O)$, a formula analogous to that for chlorine hydrate. Another point of analogy with chlorine is that a compound of water, carbon tetrachloride, and chlorine peroxide has been obtained (compare Jakowkin, Abstr., 1899, ii, 736).

It has been shown that in the reduction of chlorine peroxide, chlorite is primarily produced. The formation of this intermediate stage was demonstrated in the case of the action of chlorine peroxide on iodide, nitrite, and zinc, while its formation is very probable also in the action of chlorine peroxide on ferrous sulphate and on arsenious acid. This view of the primary production of chlorite in the reduction of chlorine peroxide is supported also by a study of the rate of decomposition of

chlorine peroxide in aqueous solution in presence of Cl' ions. It is found that the velocity of this change is proportional to the square of the concentration of the chlorine peroxide, and approximately proportional to the concentration of the Cl' ion. The decomposition is accelerated also by H' ions. The author suggests that the primary stage in the decomposition is represented by the equation

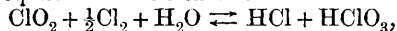


the subsequent reactions taking place with great rapidity.

Chlorous acid is a "primary oxide" (see Skrabal, *Abstr.*, 1905, ii, 18) in that it decomposes into two substances, one of which is more, the other less, highly oxidised, thus : $3\text{HClO}_2 = 2\text{HClO}_3 + \text{HCl}$, and possibly $4\text{HClO}_2 = \frac{1}{2}\text{Cl}_2 + 3\text{ClO}_2 + 2\text{H}_2\text{O}$. Like other "primary oxides," chlorous acid is a very unstable substance, but the author has succeeded in preparing solutions of the acid, taking the precaution to remove traces of hypochlorite by addition of a little arsenious acid.

The various methods available for the determination of chlorine peroxide in presence of chlorine, chloride, and chlorate are discussed, and improvements are suggested. The author, in agreement with Reyhler (*Abstr.*, 1901, ii, 548) and Oechsli (*Abstr.*, 1904, ii, 22), finds that the best method of estimating chlorine peroxide in solution is by means of potassium iodide and thiosulphate. A measured quantity of the chlorine peroxide solution is added to 50 c.c. $N/10$ or $N/5$ KI, and the mixture is then acidified with 3—5 c.c. $2N \text{H}_2\text{SO}_4$. After three minutes, the liberated iodine is titrated with $N/10 \text{Na}_2\text{S}_2\text{O}_3$. It is necessary to wait a little before titrating, because the last stages of the reaction are not completed instantaneously. J. C. P.

Reactions of Chlorine Dioxide and Chlorous Acid. WILLIAM BRAY (*Zeit. anorg. Chem.*, 1906, 48, 217—250. Compare preceding abstract).—In the dark, at the ordinary temperature, aqueous solutions of chlorine dioxide slowly decompose in approximate accordance with the equation $6\text{ClO}_2 + 3\text{H}_2\text{O} = 5\text{HClO}_3 + \text{HCl}$; at 0° , the rate is practically zero. The action is accelerated by chlorine ions and by platinum, but is practically unaffected by hydrogen and ClO_3' ions. At 60° , a little oxygen is evolved owing to splitting up of the dioxide into its elements; at 100° , in the dark, this is the chief and probably the primary reaction. The rate of decomposition is greatly increased by chlorine; the equation in this case is



which is shown to be a reversible reaction. In sunlight, as at 100° , the primary reaction is probably decomposition of the dioxide into its components.

In alkaline solution, in absence of light, chlorine dioxide decomposes with production of equivalent amounts of chlorite and chlorate. In the presence of sodium hydrogen carbonate, this action proceeds slowly; the chlorite is stable under these conditions and almost completely ionised. The chemical dynamics of the reaction between the peroxide and sodium hydroxide have been investigated, and it is shown that with excess of alkali the rate is proportional to the hydroxyl ion concentration and to the square of the dioxide concentration.

The interaction of chlorous and chloric acids in the presence of sulphuric acid has been studied with the object of determining if, as has often been assumed, there is a well-defined equilibrium $2\text{ClO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HClO}_2 + \text{HClO}_3$. It is found that the acids interact very slowly and that many other substances besides chlorine dioxide are produced; further, the proportion of chlorate continually increases, so that if the equilibrium in question is a real one it is of secondary importance.

The reaction between hydrochloric and chloric acids (from sodium chloride, sodium chlorate, and sulphuric acid) has also been studied, and it is shown, in agreement with Schacherl (this Journal, 1877, i, 47) and with earlier kinetic investigations by the author, under rather different conditions (Abstr., 1903, ii, 275), that when the chlorine ion concentration is small, the reaction proceeds according to the equation $\text{ClO}_3' + \text{Cl}' + 2\text{H} \rightleftharpoons \text{ClO}_2 + \frac{1}{2}\text{Cl}_2 + \text{H}_2\text{O}$, the reverse of that expressing the decomposition of chlorine dioxide by water in the presence of chlorine ions. With relatively concentrated hydrochloric acid, on the other hand, the change is usually assumed to proceed according to the equation $\text{HClO}_3 + 5\text{HCl} = 3\text{Cl}_2 + 3\text{H}_2\text{O}$, and in agreement with this it was found that practically no chlorine dioxide was evolved from a solution containing gram-molecular amounts of sodium chloride and sodium chlorate per litre, and normal with respect to sulphuric acid. The author regards as doubtful Sand's contention (Abstr., 1905, ii, 156) that the foregoing reaction is quinque-molecular; it is probably quadrimolecular. Reasons are given for supposing that in the first stage of the reduction of the chlorate ion the chlorite ion is formed.

G. S.

Conversion of Oxygen into Ozone at High Temperatures and the Oxidation of Nitrogen. FRANZ FISCHER and FRITZ BRAEHMAR (*Ber.*, 1906, 39, 940—968).—Ozone, like nitric oxide and hydrogen peroxide, is an endothermic substance, and should therefore be produced from oxygen at high temperatures; a satisfactory experimental proof of this statement has hitherto not been forthcoming owing to the extraordinarily rapid rate of decomposition of ozone at high temperatures (Clement, Abstr., 1904, ii, 479). The authors have succeeded not only in detecting ozone under these conditions, but also in isolating it. The principle of their method is the sudden cooling of the ozone at the moment of formation by liquid air or oxygen.

In the first set of experiments, hydrogen, carbon monoxide, acetylene, hydrogen sulphide, sulphur, wood charcoal, and wood are burnt either beneath, or at the surface of, liquid air. The latter, after its volume has been reduced to a few c.c., is filtered. In all cases except that of hydrogen sulphide, nitrogen trioxide is detected in the blue mass on the filter, whilst in every case ozone is obtained from the filtrate, after the air has boiled away, in the form of a dark blue ring, and is detected by its odour and by the production of a violet coloration with paper previously soaked in an alcoholic solution of tetramethyl-*p*-diaminodiphenylmethane (compare Arnold and Menzel, Abstr., 1902, ii, 352). Hydrogen peroxide cannot be detected in any case or when hydrogen is burnt beneath liquid oxygen.

In other experiments, the heating of liquid air or oxygen is brought

about by electrical means. A platinum wire can be maintained at a white heat beneath liquid air, but in liquid oxygen only if the wire is coated with zirconia and yttria. In both cases, and also by the use of the filament of a Nernst lamp, ozone is the only endothermic substance detected. By the action of the electric arc between platinised copper poles beneath liquid air, ozone and nitrogen trioxide are obtained. The production of these two substances by the passage of electric sparks through liquid air has previously been noted by Helbig. That the formation of ozone is due to thermal and not to photo-chemical causes is proved by immersing a quartz vessel containing a glowing Nernst filament under 10 mm. pressure in liquid air; ozone is not produced. Under similar conditions, ozone is obtained, however, by the use of a U-shaped quartz Geissler tube.

The original paper must be consulted for the discussion of these results and for the description and sketches of the apparatus.

The estimation of the ozone produced by these means in liquid air is effected by allowing a known volume of the liquid to boil away, the escaping gas being passed through a solution of potassium iodide.

Assuming that the sp. gr. of the mixture of oxygen and ozone is equal to that of liquid oxygen, the percentage weight of ozone can be calculated; the values obtained, about 1 per cent., are in good agreement with those calculated by Nernst's formula (*Zeit. Elektrochem.*, 1903, 9, 892).
C. S.

Ozone. II. STEPHAN JAHN (*Zeit. anorg. Chem.*, 1906, 48, 260—293. Compare Abstr., 1905, ii, 16).—With the object of elucidating the mechanism of the spontaneous decomposition of ozone, measurements of the rate of disappearance of this gas mixed with oxygen at different pressures have been made by a dynamical as well as by a statical method at a constant temperature of 127°. According to the former method (already employed by Clement, Abstr., 1904, ii, 479), ozonised oxygen was passed in a steady stream through a heated glass vessel and the proportion of ozone in the entering and issuing gas determined by titration. Experiments were made under atmospheric pressure and under 300 mm. pressure, and it was found that the rate of decomposition was inversely proportional to the oxygen pressure. The oxygen pressure was also varied by using air as a diluent; the results in this case were similar, but not so conclusive, owing probably to secondary reactions between ozone and nitrogen. The dependence of the rate of reaction on the oxygen pressure was confirmed by experiments carried out by a static method described by Warburg (Abstr., 1902, ii, 130), the rate of disappearance of ozone being determined from the change of pressure in a specially constructed apparatus.

These results indicate that the process in question proceeds in stages and that what is actually measured is a reaction in which a single atom of oxygen takes part. Taking into account the bimolecular character of the reaction, as proved by Warburg and by Clement (*loc. cit.*), the author considers that the first stage—probably $2O_3 = 2O_2 + 2O$ —is rapid, and that it is the reaction $O_3 + O = 2O_2$ which is actually measured.
G. S.

Allotropic Forms of Selenium. ROBERT MARC (*Ber.*, 1906, 39, 697—704).—Two distinct forms of metallic crystalline selenium exist, both of which are conductors. The variety produced by heating amorphous selenium forms grey crystals; it is labile and is converted into a more stable form at a rate which, above 170° , can be measured by the development of heat, a thermo-electric method of observing which is described. The transition of the labile into the more stable form may also be followed by the gradual increase of the electrical conductivity during the transition. The latter form, however, does not appear to be the most stable variety of selenium. When the labile form is quickly cooled, the conductivity rapidly increases until at the ordinary temperature the value is 1000—2000 times as great as initially; on remaining at the ordinary temperature, however, this variety of selenium decreases steadily in conductivity. The most stable form of selenium exists probably between 217° and 160° , when a condition of equilibrium between two modifications is attained; whether those modifications are the forms described or two other forms is uncertain.

Whilst amorphous selenium in thin layers has a red tint, the labile crystalline form is grey with a faint red tint and the more stable crystalline form is bluish-grey. Whilst the amorphous form is exceedingly brittle, the labile crystalline form is less so and the more stable crystalline form is malleable.

Traces of impurities in selenium have a great influence in retarding its crystallisation. A. McK.

Loss of Nitre in the Chamber Process. JOHN K. H. INGLIS (*J. Soc. Chem. Ind.*, 1906, 25, 149—154).—Only very small quantities of nitrogen peroxide and trioxide are reduced to nitrous oxide in the sulphuric acid chambers, and 50 per cent. of the total loss of nitre takes place owing to the incomplete absorption of the nitrogen peroxide and trioxide in the Gay Lussac tower.

Samples of flue gases consisting of nitrogen, oxygen, carbon dioxide, nitrous oxide, nitric oxide, nitrogen trioxide, nitrogen peroxide, sulphur dioxide, sulphur trioxide, and the vapour of sulphuric acid were analysed by liquefaction and subsequent fractional distillation. For details of the method, the original paper should be consulted.

P. H.

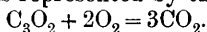
Removal of Nitrous Acid from Concentrated Nitric and Sulphuric Acids. OSWALD SILBERRAD and BERTRAM J. SMART (*J. Soc. Chem. Ind.*, 1906, 25, 156—157).—It was found that carbamide, lead peroxide, oxamide, methylamine nitrate, or aminoguanidine nitrate, which react readily with nitrous acid in aqueous solution, are very inert towards nitrous acid in presence of concentrated nitric acid either alone or in admixture with sulphuric acid; hydrazine sulphate, however, reacts with explosive violence. P. H.

Existence of Sulphides of Phosphorus. HENRI GIRAN (*Compt. rend.*, 1906, 142, 398—400).—Mixtures of sulphur and phosphorus in different proportions were heated in small sealed tubes at about 200° . After the contents had been solidified by cooling, the tubes

were gradually heated and the temperature at which complete liquefaction took place was determined. The formation of four different compounds is indicated by four temperature maxima on the curves representing the dependence of the liquefaction temperature on the composition. The maximum temperatures are 167° , 296° , 272° , and 314° , the corresponding composition being expressed by the formulæ P_4S_3 , P_2S_3 , P_2S_5 , and PS_6 respectively. The four eutectics at -40° , $+46^{\circ}$, $+230^{\circ}$, and $+243^{\circ}$ correspond approximately with the compositions P_2S , PS , PS_2 , and PS_3 respectively. The mixtures of sulphur and phosphorus, which are liquid at the ordinary temperature, exhibit supercooling to a marked degree; solidification can only be brought about by cooling to about -80° .

H. M. D.

Carbon Suboxide. I. OTTO DIELS and BERTRAM WOLF (*Ber.*, 1906, **39**, 689—697).—A *suboxide* of carbon, $O:C:C:C:O$, is formed when ethyl malonate is slowly distilled under reduced pressure into a vessel containing glass wool and a large excess of phosphoric oxide and kept at a temperature of about 300° . The products of decomposition are passed through a dry tube in order to retain small amounts of the ethyl ester, and then into a glass vessel surrounded by liquid air, where both ethylene and carbon suboxide are condensed. Part of the suboxide decomposes and forms a carmine-red deposit on the phosphoric oxide, and thus prevents the decomposition of further quantities of ethyl malonate. The ethylene volatilises readily from the mixture at the ordinary temperature, leaving a small quantity of colourless liquid. This residue can then be volatilised and collected in a tube cooled to -60° to -70° . The pure oxide is a colourless, extremely mobile refractive liquid, with an intense odour resembling acetaldehyde and mustard oil and has poisonous properties. It boils at 7° under 761 mm. pressure and has a high vapour pressure at temperatures much below its boiling point. Its vapour density accords with the formula C_3O_2 . It burns with a bright blue but at the same time smoky flame. Its combustion with oxygen is represented by the equation



Its chemical properties are those of a malonic anhydride. It combines readily with water, yielding malonic acid; with aniline to form malonanilide; with ammonia to form malonamide, and with dry hydrogen chloride to form malonyl chloride.

When kept in a sealed tube for one to two days at 15° , it gradually changes to a dark red solid mass, which dissolves in cold water to an eosin-red solution. The transformation occurs much more readily at 37° and is instantaneous at 100° .

J. J. S.

Suboxides of Carbon. MARCELLIN BERTHELOT (*Compt. rend.*, 1906, **142**, 533—537).—The name *carbon suboxide* applied by Diels and Wolf to the compound C_3O_2 (preceding abstract) is not justified, as it ignores the existence of the suboxides of carbon already described (Brodie, *Abstr.*, 1873, 348; Berthelot, *Ann. Chim. Phys.*, 1877, [v], **10**, 72; *Abstr.*, 1891, 801).

M. A. W.

The So-called Metalammonium Compounds. OTTO RUFF and EMIL GEISEL (*Ber.*, 1906, 39, 828—843. Compare Joannis, this vol., ii, 161).—The substances described by Joannis are not definite compounds of metal and ammonia, but are mixtures of the metal with its saturated solution in ammonia. This has been proved by taking a mixture in which the ratio, metal : $\text{NH}_3 = 1 : 0.9$ approx., and pressing this at a low temperature between linen; a certain amount of liquid (saturated solution) is thus pressed out, and a compact metallic mass is left.

The following values express the number of gram-molecules of ammonia required to dissolve 1 gram-atom of potassium, sodium, or lithium at the temperatures named.

	Temp... +22°.	0°.	-25°.	-30°.	-50°.	-70°.	-80°.	-100°.	-105°.
Potassium	—	4.74	—	—	4.79	—	—	4.82	—
Sodium	6.14	5.87	—	5.52	5.39	5.20	—	—	4.98
Lithium	—	3.93	3.93	—	3.93	—	3.93	—	—

No solid or liquid phase has been established in addition to the metal and its saturated solution.

The solutions of all the alkali metals in ammonia decompose more or less slowly when kept in tubes at the ordinary temperature. Hydrogen is evolved and the metallic amide is formed. Half saturated solutions require the lapse of the following times before they are completely decomposed: caesium, one to two hours; rubidium, six to ten hours; potassium, two to three days; sodium and lithium, two to three weeks. Increase of temperature facilitates the decomposition. The alkali hydrides also react with liquid ammonia, yielding hydrogen and the metalamide.

J. J. S.

Preparation of Alkali Hydroxides by means of Alkali Silicofluorides. JULIUS A. REICH (D.R.-P. 161795).—In the decomposition of alkali silicofluorides by means of lime according to the equation $\text{Na}_2\text{SiF}_6 + 4\text{CaO} = \text{Na}_2\text{O} + 3\text{CaF}_2 + \text{CaSiO}_3$, the residue is not readily soluble in hydrochloric acid, and the recovery of the hydrofluosilicic acid is thus difficult and incomplete. This is avoided by using about double the quantity of lime indicated by the above equation, the excess of lime being either added at first or after the removal of the alkali hydroxide. The residue dissolves readily in hydrochloric acid, and the hydrofluosilicic acid is then precipitated by potassium chloride.

C. H. D.

Behaviour on Impact of Chemical Elements, especially of Light Metals. O. OHMANN (*Ber.*, 1906, 39, 866—870. Compare Doermer, this vol., ii, 162).—Doermer ascribes the sparking of metallic calcium when hit with an iron hammer on an iron anvil to the presence of rust; the author disagrees with this view, since granite or quartz may be substituted for iron with a like effect. According to the author, the sparking observed when calcium is detonated is due to evaporation of the metal and subsequent chemical action. When the detonation is conducted in an atmosphere of oxygen, the light evolved is more intense than in air.

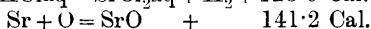
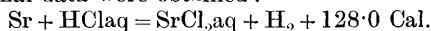
The behaviour of sodium, potassium, lithium, and phosphorus on impact is similar, although varying in degree. The effect with magnesium and aluminium is but slight.

A. McK.

Iron and Calcium. C. QUASEBART (*Metallurgie*, 1906, 3, 28—29).—Calcium is now frequently employed for the deoxidation of iron, the reaction taking place with great development of heat. Calcium does not alloy with iron, whether containing carbon or not. In one experiment, a hollow iron cylinder filled with calcium was heated at 1400° for three and a half hours without any absorption of calcium by the iron taking place.

C. H. D.

Preparation and Properties of Strontium. ANTOINE GUNTZ and ROEDERER (*Compt. rend.*, 1906, 142, 400—401).—Pure strontium was obtained by heating the hydride at 1000° in a vacuum, the strontium vapour being condensed in a cooled steel tube. Analysis of the product gave 99.43 per cent. of strontium. It has a silver-white colour, but tarnishes immediately in contact with the air, melts at about 800° , and volatilises at a somewhat higher temperature. Dry carbon dioxide has no action on it in the cold; at a red heat, the gas is absorbed with formation of strontium carbide and carbonate. It is attacked by water and ethyl alcohol with evolution of hydrogen. The following thermal data were obtained:



Thomsen found 117.05 Cal. for the heat of solution of an impure specimen of strontium in dilute hydrochloric acid. The heats of formation of strontium compounds recorded by him are consequently too small to the extent of 11.0 Cal.

H. M. D.

Magnesium Permanganate as an Oxidising Agent. ARTHUR MICHAEL and WIGHTMAN W. GARNER (*Amer. Chem. J.*, 1906, 35, 267—271).—Magnesium permanganate dissolves in methyl alcohol, forming a solution which is fairly stable at the ordinary temperature, but it readily attacks ethyl and propyl alcohols. The salt is soluble in glacial acetic acid and in methyl and ethyl acetates, and yields comparatively stable solutions. Propionic acid is slowly attacked by the salt, whilst butyric and isovaleric acids are violently decomposed with evolution of carbon dioxide. The salt dissolves in acetone, but a reaction immediately takes place with development of heat. Glacial acetic acid and pyridine are the only solvents which are found to be sufficiently stable towards the salt to be of practical use for oxidation purposes. Benzene and its homologues are readily attacked by a solution of magnesium permanganate in glacial acetic acid, with evolution of carbon dioxide. Open-chain hydrocarbons, such as hexane, undergo similar oxidation.

Magnesium permanganate is more soluble in pyridine than in glacial acetic acid, but the solution in the former solvent has much weaker oxidising powers. It is suggested that the aqueous solution of the salt would be serviceable for the oxidation of difficultly oxidisable substances and also for cases in which it is desirable to prevent the formation of an alkaline solution.

E. G.

Lead and Arsenic. K. FRIEDRICH (*Metallurgie*, 1906, 3, 41—52).—Alloys containing 0—34·4 per cent. of arsenic have been prepared and examined, the preparation of alloys richer in arsenic not being found possible. Partial separation of lead takes place in the liquid state. The freezing-point curve consists of two branches only, the eutectic point occurring at 292° and 2·5—3 per cent. of arsenic. The probable course of the curve, allowance being made for the separation of the liquid into layers, is discussed. Microscopic examination shows the presence of lead, arsenic, and the eutectic only. There is no evidence of the existence of the compounds Pb_3As_4 , $PbAs$, Pb_4As_3 , or Pb_2As (Descamps, *Abstr.*, 1878, 705), or of Pb_3As_2 (Spring, *Abstr.*, 1883, 650).
C. H. D.

Some Metals and Minerals found in the Excavations of the Tell Acropolis of Susa in Persia. MARCELLIN BERTHELOT and GUSTAVE ANDRÉ (*Compt. rend.*, 1906, 142, 473—480. Compare *Abstr.*, 1901, ii, 514, 515; 1902, ii, 261, 397; 1905, ii, 164).—The original contains a description and analysis of fifteen metallic fragments obtained from the excavations at Susa and dating from 1000 to 750 B.C. A silver vase in which all the silver was in the form of chloride contained 1·12 per cent. of gold. Five of the eleven bronze objects examined contained nickel, and the lead fragments consisted of pure lead or fused litharge or lead silicate.
M. A. W.

Copper and Sulphur. E. HEYN and O. BAUER (*Metallurgie*, 1906, 3, 73—86).—Cuprous sulphide and copper are not perfectly miscible in the molten condition, mixtures containing from 9 to 85 per cent. of Cu_2S separating into two liquid layers. The freezing-point curve falls from 1127° , the freezing point of cuprous sulphide, to 1102° , then remaining horizontal until the disappearance of one liquid phase, and afterwards falling to the eutectic temperature, 1067° , then rising again to 1085° , the freezing point of copper. The eutectic contains 3·82 per cent. of cuprous sulphide.

Sulphur dioxide is without action on copper at 900 — 1100° , except in presence of a reducing agent, such as carbon, in which case cuprous sulphide is formed. At this temperature the reaction $Cu_2S + 2Cu_2O = SO_2 + 6Cu$ is complete.

Selenium and tellurium when added to copper give rise to a micro-structure quite similar to that produced by sulphur. The following delicate test may be used to distinguish them. Turnings of the alloy are warmed with a 10 per cent. solution of potassium cyanide, a little alcohol is then added, and then a solution prepared by dissolving 25 grams of cadmium acetate in 200 grams of acetic acid and diluting to a litre with water. Even minute quantities of cuprous sulphide cause a yellow precipitate, selenium causes an orange precipitate. In the case of tellurium, the addition of potassium cyanide alone causes a red coloration, similar to that of permanganate; cadmium acetate and alcohol then give a greyish-black precipitate. Ferrous sulphide does not give this reaction.

The paper is illustrated by a number of micro-photographs.

C. H. D.

Cuprammonium Salts. DAVID W. HORN (*Amer. Chem. J.*, 1906, **35**, 271—286).—The preparation and properties of the following salts are described: $\text{CuC}_2\text{O}_4 \cdot 2\text{NH}_3 \cdot 2\text{H}_2\text{O}$; $\text{CuC}_2\text{O}_4 \cdot 5\text{NH}_3$; $\text{CuC}_2\text{O}_4 \cdot 4\text{NH}_3 \cdot 2\text{H}_2\text{O}$; $\text{CuC}_2\text{O}_4 \cdot 2\text{NH}_3$; and $\text{CuC}_2\text{O}_4 \cdot \text{NH}_3$. The first of these has been described previously by Vogel and by Seubert and Rauter (*Abstr.*, 1892, 1431). The bearing of these salts on the question of types of cuprammonium compounds is discussed. E. G.

Double Salts of Mercuric Chloride with the Alkali Chlorides and their Solubility. HARRY W. FOOTE and L. H. LEVY (*Amer. Chem. J.*, 1906, **35**, 236—246).—The solubility method of investigating the double salts formed in mixtures of two single salts (*Abstr.*, 1903, i, 797) has been applied to the double salts of mercuric chloride with potassium, sodium, and rubidium chlorides. The caesium mercuric chlorides have been studied previously (*Abstr.*, 1903, ii, 728). The following results have been obtained.

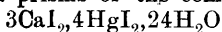
The three potassium mercuric chlorides, $2\text{KCl} \cdot \text{HgCl}_2 \cdot \text{H}_2\text{O}$; $\text{KCl} \cdot \text{HgCl}_2 \cdot \text{H}_2\text{O}$, and $\text{KCl} \cdot 2\text{HgCl}_2 \cdot 2\text{H}_2\text{O}$, described by Bonsdorf (*Ann. Phys. Chem.*, 1829, [ii], **17**, 115), are found to exist at 25°.

Two sodium mercuric chlorides, $2\text{NaCl} \cdot \text{HgCl}_2$ and $\text{NaCl} \cdot \text{HgCl}_2 \cdot 2\text{H}_2\text{O}$, have been described by Bonsdorf (*loc. cit.*). The existence of the latter salt has been confirmed, but it has been found that the former salt does not exist between 10·3° and 25°.

The five following rubidium mercuric chlorides are formed at 25°: $\text{RbCl} \cdot 5\text{HgCl}_2$; $3\text{RbCl} \cdot 4\text{HgCl}_2 \cdot \text{H}_2\text{O}$; $\text{RbCl} \cdot \text{HgCl}_2 \cdot \text{H}_2\text{O}$; $3\text{RbCl} \cdot 2\text{HgCl}_2 \cdot 2\text{H}_2\text{O}$, and $2\text{RbCl} \cdot \text{HgCl}_2 \cdot \text{H}_2\text{O}$. No evidence was obtained of the existence of the salts $2\text{RbCl} \cdot \text{HgCl}_2$; $2\text{RbCl} \cdot \text{HgCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{RbCl} \cdot \text{HgCl}_2$, described by Godeffroy (*Arch. Pharm.*, 1878, [iii], **12**, 47). The double salts, $2\text{RbCl} \cdot \text{HgCl}_2 \cdot \text{H}_2\text{O}$ and $3\text{RbCl} \cdot 4\text{HgCl}_2 \cdot \text{H}_2\text{O}$, were isolated and analysed; the former yields large, well-defined crystals and the latter crystallises in silky needles.

The solubilities of the mercuric alkali chlorides are plotted as a curve, and an account is given of the behaviour of the various salts on recrystallisation. E. G.

Double Iodides of Mercury and Calcium. ANDRÉ DUBOIN (*Compt. rend.*, 1906, **142**, 395—398).—When calcium and mercuric iodides are alternately dissolved in water until the saturation point is reached, a solution of the composition $\text{CaI}_2 \cdot 1 \cdot 30\text{HgI}_2 \cdot 12 \cdot 30\text{H}_2\text{O}$ and sp. gr. 2·89 at 15·9° is obtained. On cooling slightly, large, deliquescent, yellow crystals of the formula $\text{CaI}_2 \cdot \text{HgI}_2 \cdot 8\text{H}_2\text{O}$ are deposited. These dissolve in water and many organic solvents without decomposition; the sp. gr. at 0° is 3·258 to 3·337. If the mother liquor is warmed and more mercuric iodide dissolved, then on cooling to 0° small crystals of the composition $\text{CaI}_2 \cdot 5\text{HgI}_2 \cdot 8\text{H}_2\text{O}$ are obtained. In contact with water and certain organic liquids, this substance decomposes with separation of mercuric iodide. If the solution previously mentioned is cooled below 0°, then, in addition to these small crystals, large, elongated prisms of the composition



separate. In contact with water, mercuric iodide separates, but it

dissolves readily in alcohols, glycerol, ethyl acetate, acetone, aniline, and other organic liquids. Its sp. gr. at 0° is 3.56 to 3.66.

H. M. D.

Compounds of the Rare Metals of the Cerium Group. CAMILLE MATIGNON (*Compt. rend.*, 1906, 142, 394—395).—A claim for priority (compare Brill, this vol., ii, 27).

H. M. D.

Boiling and Distillation of Nickel, Iron, Manganese, Chromium, Molybdenum, Tungsten, and Uranium. HENRI MOISSAN (*Compt. rend.*, 1906, 142, 425—430. Compare this vol., ii, 92, 175).—The metals of the iron group can be distilled in the electric furnace, yielding crystalline distillates which have the same chemical properties as the finely-powdered metals. The metals differ greatly in their boiling points: manganese is the most volatile, then follow, in order, nickel, chromium, iron, and uranium, molybdenum and tungsten being the most refractory. The distillation of iron presents the greatest difficulty owing to the tumultuous frothing caused by the boiling metal evolving the gas occluded by the fused metal; a similar phenomenon is exhibited by molybdenum.

M. A. W.

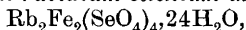
Iron-carbon Alloys of High Carbon Content. F. WÜST (*Metallurgie*, 1906, 3, 1—13).—The theory of Roozeboom (Abstr., 1900, ii, 728) is found to break down in the case of iron-carbon alloys of high carbon content, as has been pointed out by Heyn (Abstr., 1904, ii, 737). When the freezing point of iron has been depressed to 1130° by the addition of carbon, further increase of carbon does not produce any further change of freezing point, and graphite does not separate from the liquid solution. A development of heat in cooling between 1130° and 700° could not be recognised. Microscopic examination of alloys cooled from different temperatures shows that cementite is first formed on solidification, but ceases to be the stable form below 1000°. Below 700°, it is metastable, and does not break up on prolonged heating. The final state of equilibrium is ferrite + graphite. The possible constitution of martensite, troostite, and sorbite is also discussed.

C. H. D.

Influence of Phosphorus on the Solubility of Carbon in Iron. F. FETTWEIS (*Metallurgie*, 1906, 3, 60—62).—The experiments were carried out by adding iron phosphide to a pure Swedish cast iron in a magnesia crucible. The quantity of carbon dissolved by iron diminishes with increasing phosphorus, falling by about 0.5 per cent. for each additional 2 per cent. of phosphorus. Iron phosphide appears to dissolve a certain amount of carbon, but the condition in which it is retained is undetermined.

C. H. D.

Selenium-iron Alums. CESARE RONCAGLIOLO (*Gazzetta*, 1905, 35, ii, 553—562).—*Iron rubidium selenium-alum*,



prepared by dissolving freshly-precipitated ferric hydroxide in excess of selenic acid solution and adding the calculated amount of rubidium

carbonate, separates in pale violet crystals belonging to the regular system and melts at $40-45^\circ$ in its water of crystallisation, giving a red liquid. It has a sp. gr. 2.1308 at 15° , and at 18° its index of refraction is 1.50473 for the medium red, 1.50699 for the D lines, 1.51190 for the medium green, 1.51725 for the medium blue, and 1.52290 for the medium violet.

Iron caesium selenium-alum, $\text{Cs}_2\text{Fe}_2(\text{SeO}_4)_4 \cdot 24\text{H}_2\text{O}$, forms violet crystals of the regular system and melts at $55-60^\circ$ in its water of crystallisation. It has a sp. gr. 3.6176 at 15° , and its index of refraction is 1.50884 for the mean red, 1.51164 for the D lines, 1.51615 for the mean green, 1.52092 for the mean blue, and 1.52645 for the mean violet. If, in the preparation of this alum, the solution is heated excessively, a greenish-yellow, amorphous basic selenate of iron and caesium is deposited.

T. H. P.

Constitution of Chromic Sulphates. ALBERT COLSON (*Compt. rend.*, 1906, 142, 402—404).—When the green solution obtained by saturating chromic acid solution at -4° with sulphur dioxide is at once evaporated in a vacuum, crystals of the composition $\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ are deposited. From the data obtained for the heat change when barium chloride is added to the freshly-prepared solution of the sulphate and to the solution which has been kept for twenty-four hours, it is concluded that none of the sulphuric acid of the original substance is precipitated by barium chloride, but that this substance rapidly changes into the green sulphate previously described, two-thirds of the sulphuric acid of which is precipitated by barium chloride (compare Abstr., 1905, ii, 460). As this change proceeds, the volume of the solution diminishes considerably, and from the amount of this contraction the author supposes that one molecule of water enters the molecule of the sulphate for each SO_4 group which becomes precipitable by barium chloride. According to this view, the violet sulphate would be represented by $\text{Cr}_2(\text{SO}_4)_3(\text{H}_2\text{O})_3$.

When a mixture of 2 mols. of chromic acid and 3 mols. of sulphuric acid is dissolved in its own weight of water and the solution saturated with sulphur dioxide, a green substance, supposed to have the composition $\text{Cr}_2(\text{OH})_2(\text{SO}_4\text{H})_4 \cdot 10\text{H}_2\text{O}$, is obtained.

H. M. D.

Two Isomeric Chromium Chloro-sulphates. RUDOLF F. WEINLAND and REINHOLD KREBS (*Zeit. anorg. Chem.*, 1906, 48, 251—259).—From an aqueous solution of green hydrated chromium chloride to which a molecular quantity of sulphuric acid has been added, a salt of the formula $\text{CrClSO}_4 \cdot 8\text{H}_2\text{O}$ separates slowly in green needles when kept for a few days in a desiccator. From the bluish-grey hydrated chromium chloride, an isomeric compound has been obtained in a similar manner; it occurs in violet, flattish needles or in nearly rectangular plates. A green salt, apparently identical with the above except that it crystallises with $6\text{H}_2\text{O}$, has already been described by Schiff and by Recoura (see Abstr., 1902, ii, 563).

In an acidified solution of the green salt at 0° , neither silver nitrate nor barium chloride produce an immediate precipitate, whereas the chloride, but not the sulphate, is immediately thrown down from an

acidified solution of the violet salt. In a neutral solution of the green salt at 0° , half the chlorine is immediately precipitated by silver nitrate, whilst the whole of the sulphate is thrown down by barium chloride. The authors consider that in aqueous solution the green salt is not ionised, whilst the violet salt is split up into two ions, and they have confirmed this conclusion by cryoscopic observations. In a vacuum over sulphuric acid, the green salt loses three molecules and the violet salt two molecules of water; contrary to the view of Recoura (*loc. cit.*), this dehydration is in neither case attended with a change of function of the acid groups.

In accordance with their behaviour, the formula



is ascribed to the green salt and that of $[\text{CrSO}_4(6\text{H}_2\text{O}), 2\text{H}_2\text{O}]\text{Cl}$ to the violet salt. G. S.

Preparation of Antimony Oxide from Antimony Sulphide. SIEGMUND METZL (D.R.-P. 161776).—Antimony trisulphide is only incompletely converted into sulphate by concentrated sulphuric acid at 300° , and the product, being mixed with sulphur, is unsuitable for the preparation of oxide. Dilute sulphuric acid to which an alkali sulphate has been added, however, converts the sulphide completely into sulphate at 130° , all the sulphur being evolved as sulphur dioxide and the antimony separating in the form of a crystalline double sulphate. The crystals are separated and boiled with water, pure antimony trioxide being obtained and the sulphuric acid and alkali sulphate regenerated. The method may also be applied to antimony sulphide ores. Magnesium sulphate may replace the alkali sulphate.

C. H. D.

Peroxides of Bismuth. II. ALEXANDER GUTBIER and R. BÜNZ (*Zeit. anorg. Chem.*, 1906, **48**, 294—296. Compare this vol., ii, 174; Deichler, 1899, ii, 428).—Deichler (*loc. cit.*) claimed to have obtained pure homogeneous "potassium bismuthate" by electrolysis of a mixture of bismuth oxide, potassium hydroxide, and potassium chloride and washing the deposit with ice-cold water. The authors have repeated his experiments, but have been unable to obtain a homogeneous substance; they regard the products obtained by electrolysis as identical with those prepared by the use of gaseous chlorine and consider that there is no evidence of the existence of "potassium bismuthate" or "bismuthic acid."

G. S.

Mineralogical Chemistry.

Petroleum from the Mayaro-Guayaguayare District, Trinidad (*Bull. Imp. Inst.*, 1905, 3, 32—38).—Five samples of crude petroleum have been examined and the flash points have been determined by the Abel-Pensky method. Sample 1, from a well near Pilot River, consisted of a black, opaque oil. Sample

2, obtained from another well in the same vicinity, was a dark brown, nearly opaque, rather viscous oil. Sample 3, from a well near Grand Caille Point, was an opaque oil resembling sample 2 in appearance and contained a large percentage of solid paraffin hydrocarbons. Sample 4, from a well on the coast, north of Benitie Road, was of similar character to samples 2 and 3, but more viscous. Sample L. S., from the Lizard Spring, also resembled samples 2 and 3. The results of the examination of these samples are summarised in the following table.

	1.	2.	3.	4.	L. S.
Oil boiling below 150° ("light petroleum"), per cent.	23.0	12.0	7.6	1.0	1.0
Oil boiling at 150—300° ("kerosene"), per cent.	39.5	30.0	43.1	21.0	54.0
Heavy oil boiling above 300° (distilled under reduced pressure), per cent.	33.0	46.6	44.6	73.2	35.4
Coke and loss, per cent.	4.5	11.4	3.7	4.6	9.6
			(water, 1 per cent.)		
Sp. gr. of crude oil at 17°	0.894	0.913	0.856	0.933	0.900
Flash point of crude oil	2.0°	9.0°	19.5°	about 84°	60.0°

It is shown that a relation exists between the percentage of light oil in the petroleum from the different wells and the geological structure of the country in which the latter are situated. E. G.

Composition and Properties of Mineral Pitch from Ijebu District, Lagos (*Bull. Imp. Inst.*, 1905, 3, 39—40).—The sample consisted of rather soft, adhesive pitch which had an unpleasant odour, melted almost completely at 65°, contained patches of earth consisting of clear quartz grains embedded in decomposed organic matter, and had the following composition: portion soluble in acetone ("petroleum"), 39.13 per cent.; portion soluble in chloroform but insoluble in acetone ("asphaltene"), 19.67 per cent.; non-bituminous organic matter and combined water (by difference), 6.75 per cent.; ash, 32.83 per cent.; moisture, 1.62 per cent. Analysis of the ash gave:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.
89.49	7.39	1.50	1.08	0.22

E. G.

Fluid Enclosures of Alpine Quartz Crystals. JOHANNES KÖNIGSBERGER and W. J. MÜLLER (*Centr. Min.*, 1906, 72—77).—The gas-bubbles in the minute cavities of quartz crystals from the crevices in the protogine of the Swiss Alps disappear at temperatures of 199—210°, 215—222°, and 223—229°, these intervals being the temperatures at which the first and last bubbles disappear in one and the same crystal. The disappearance of the bubbles is due to the expanding liquid completely filling the cavity. When ignited, the quartz decrepitates and there is a loss of 0.17 to 0.19 per cent. of water and carbon dioxide. In different crystals, the ratio H₂O : CO₂ varied from 92 : 8 to 83 : 17. After ignition, the quartz was digested with water for the purpose of dissolving out and analysing the salts which had been held in solution in the liquid of the cavities. The

following figures give the composition of the liquid enclosures of a crystal from Bächistock :

H ₂ O.	CO ₂ .	Na.	K.	Li.	Ca.	Cl.	SO ₄ .	O ₃ .
83.4	9.5	2.0	0.7	0.2?	0.3	1.6	0.5	1.8

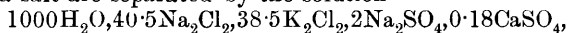
This may be taken as representing the composition of the solvent from which the minerals in the crystal-lined crevices grew, and in this connection the presence of alkali salts is of significance.

L. J. S.

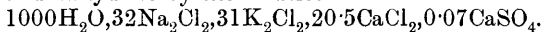
Tinstone from Madagascar (*Bull. Imp. Inst.*, 1905, 3, 41).—This mineral consisted of massive tinstone and gave the following results on analysis: SnO₂, 97.98 per cent.; Fe₂O₃, 0.15 per cent.; CaO, 0.20 per cent.; insoluble residue (principally niobic and tantallic oxides), 1.55 per cent.

E. G.

Formation of Oceanic Salt Deposits. XLVI. Anhydrite, Syngenite, Glauberite, and Penta-salt at 83°, and the Formation of Calcium Chloride and Tachhydrite. JACOBUS H. VAN'T HOFF, P. FARUP, and J. D'ANS (*Sitzungsber. K. Akad. Wiss. Berlin*, 1906, 6, 218—224. Compare Abstr., 1903, ii, 143, 368, 434, 555; 1904, ii, 417, 492).—The composition of the saturated solutions which limit the deposition of anhydrite, syngenite, glauberite, and penta-salt at 83° has been determined. The limiting solution for the pair, anhydrite, glauberite, is situated in the kieserite region, and its composition is 1000H₂O, 18Na₂Cl₂, 47.5MgCl₂, 13.5MgSO₄, 0.28CaSO₄. That for glauberite and syngenite is in the glaserite region and of the composition 1000H₂O, 40.5Na₂Cl₂, 33.5K₂Cl₂, 6.5Na₂SO₄. Syngenite and penta-salt are separated by the solution



penta-salt and anhydrite by the solution



In determining the composition of the last solution it was found that double decomposition between anhydrite and potassium chloride takes place according to the equation $6\text{CaSO}_4 + 2\text{KCl} + \text{H}_2\text{O} = \text{K}_2\text{SO}_4 + 5\text{CaSO}_4 + \text{H}_2\text{O} + \text{CaCl}_2$. This transformation accounts for the greatly increased percentage of calcium in this solution.

H. M. D.

Two New Mineral Phosphates from Russia. S. P. POPOFF (*Centr. Min.*, 1906, 112—113).—The new minerals occur in the beds of limonite ore on either side of the Straits of Kerch, namely, in the Kerch Peninsula, Crimea, and at Taman.

Paravivianite, (Fe, Mn, Mg)₃P₂O₈·8H₂O, differs from vivianite in containing some manganese and magnesium replacing iron (anal. I). The radially arranged crystals are transparent, and blue in colour.

Kertschenite, (Fe, Mn, Mg)O, Fe₂O₃·P₂O₅·7H₂O, is found as dark green, almost black, flattened crystals, forming radially fibrous aggregates (anal. II).

	P ₂ O ₅ .	FeO.	Fe ₂ O ₃ .	MnO.	MgO.	CaO.	H ₂ O.	Total.	Sp. gr.
I.	27·01	39·12	0·00	2·01	1·92	0·48	29·41	100·00	2·66—2·67
II.	28·20	9·49	32·93	1·92	1·55	0·47	24·98	99·54	2·65

L. J. S.

Loss on Ignition as a Mineralogical Character. VICTOR GOLDSCHMIDT (*Jahrb. Min.*, 1906, i, 16—19).—The loss in weight when a mineral is ignited is a definite quantity, which may be readily determined, and its use as a character of determinative value is recommended. It is necessary to state the conditions of heating—whether over a spirit-lamp, blowpipe, in an electric furnace or muffle, or whether the mineral is enclosed in a borax or silicate fusion. In most cases the loss in weight corresponds with the amount of water contained in the mineral, although sometimes other substances (mercury, sulphur, ammonia, &c.) may be expelled; in certain cases, as when iron is oxidised, there may be an increase in weight. It is proposed to give determinations of this character for different groups of minerals (compare following abstract). L. J. S.

Loss on Ignition of Zeolites as Mineralogical Characters. VICTOR GOLDSCHMIDT and P. HERMANN (*Jahrb. Min.*, 1906, i, 20—26. Compare preceding abstract).—Various zeolites, in small fragments, were heated, 30—100 mg. at a time, in a platinum spoon over a spirit-lamp, and at the end of each ten minutes the loss in weight determined on a balance weighing to 1 mg.; a constant weight was, as a rule, obtained after the second heating. The results so obtained for 18 species of zeolites and for datolite, pectolite, and prehnite are stated. The loss in each case agrees with the percentage of water contained in the minerals. L. J. S.

Physiological Chemistry.

Cheyne-Stokes Breathing. MARCUS S. PEMBREY, ARTHUR P. BEDDARD, and H. FRENCH (*Proc. Physiol. Soc.*, 1905-6, vi—viii; *J. Physiol.*, 34. Compare Abstr., 1905, ii, 263).—Administration of oxygen in two cases of Cheyne-Stokes breathing caused the breathing to become continuous. Air containing 4.67 per cent. of carbon dioxide almost abolished the apnoëic pauses. The blood-pressure is rather higher during the periods of hyperpnœa. W. D. H.

Respiration of Heart, with Special Reference to the Heart of Limulus. H. H. NEWMAN (*Amer. J. Physiol.*, 1906, 15, 371—386).—The heart ganglion is comparatively indifferent to lack of oxygen. Hydrogen exercises a favourable influence on cardiac rhythm. The heart ganglion is very sensitive to carbon dioxide, and shows a primary stimulation followed by a quick fall to diastolic standstill. Recovery

is rapid. The heart muscle is very much less sensitive to carbon dioxide. The heart ganglion is much more resistant to lack of oxygen than is the central nervous system. Asphyxia is believed to be due to an accumulation of carbon dioxide produced by the activity of both muscular and ganglionic elements of the heart, but affecting chiefly the ganglionic element. W. D. H.

Absorption and Consumption of Oxygen in Heart Tissue. E. G. MARTIN (*Amer. J. Physiol.*, 1906, 15, 303—320).—Experiments on strips of turtle's ventricles show that they soon cease beating in solutions free from oxygen. Oxygenation easily induces recovery, whereas the addition of calcium to a sodium chloride solution free from oxygen does not. The excellent recovery which follows the addition of a calcium salt to a solution containing oxygen indicates that the ability of the cardiac tissue to absorb oxygen from the surrounding medium is dependent on the presence within it of calcium ions. In alkaline solutions, the effect is explained by supposing that the alkali decomposes some substance containing oxygen in the tissue, and thereby a definite store of oxygen is available which is not affected by other modes of treatment. W. D. H.

The Glycuronic Acid of the Blood Corpuscles. RAPHAEL LÉPINE and BOULUD (*Compt. rend.*, 1906, 142, 196—199. Compare Abstr., 1904, ii, 422; 1905, ii, 730).—The glycuronic acid in the blood of the dog and man is contained mainly in the corpuscles; it is only in the layer of serum nearest the corpuscles in centrifugalised blood that any is found. Glycolysis, which may occur even during centrifugalisation, leads to a lessening, and ultimately to the disappearance, of the acid. W. D. H.

Catalases of the Blood. LEOPOLD VAN ITALLIE (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 8, 623—628).—Blood from various animals was heated for half an hour at 63° (compare Senter, Abstr., 1903, ii, 661), cooled to 15°, and mixed with hydrogen peroxide solution, when the presence of active catalase was indicated by the evolution of oxygen. Human and monkey blood appeared still to contain catalase, which was shown to be absent in the blood of horses, oxen, pigs, goats, sheep, rabbits, rats, hares, chickens, pigeons, fish, and frogs. The results suggest that the catalases occurring in the blood of different species of animals are not identical. E. F. A.

Adaptation of the Salivary Secretion to Diet. C. HUGH NEILSON and OLIVER P. TERRY (*Amer. J. Physiol.*, 1906, 15, 406—411).—Dogs' saliva contains an active ptyalin, but is relatively inert compared to human saliva. Like the other secretions (for example, that of the pancreas), there is an adaptation to diet; the saliva and extracts of the salivary glands of dogs fed on bread is more strongly amylolytic than that from those fed on meat. W. D. H.

Gastric Secretion. J. SYDNEY EDKINS (*J. Physiol.*, 1906, 34, 133—144. Compare Abstr., 1905, ii, 730).—Extracts of pyloric

mucous membrane in boiling water with 0.4 per cent. hydrochloric acid contain a substance which, on injection into the blood-vessels of an animal, leads to the secretion of gastric juice. Extracts made with cold water, peptone, dextrose, or glycerol contain variable amounts of the same material. Extracts of the fundus mucous membrane do not contain it. Some inactive extracts of pyloric or true cardiac mucous membrane can be activated by boiling or by treatment with acid. This is not so for the inactive extracts of the fundus. Atropine does not diminish the reaction of an animal to this excitant. The substance is not a ferment, for boiling increases rather than lessens its activity.

W. D. H.

Digestion in the Horse when Fed on Maize. ARTHUR SCHEUNERT and WALTHER GRIMMER (*Zeit. physiol. Chem.*, 1906, 47, 88—125. Compare Abstr., 1905, ii, 733).—The digestive contents in the horse when fed on maize show great variations; the amount of water in the stomach is usually high and the reaction there is alkaline. There is a considerable amount of lactic acid and similar fermentation occurring in the intestinal contents. Passage into the cæcum begins early. Digestion of carbohydrate in the stomach is slow, as in feeding on oats, whereas proteid digestion is more rapid than with oats. Absorption is fairly large in the stomach, but is larger in the small intestine.

W. D. H.

Adaptation of the Pancreas to Lactose. R. H. ADERS PLIMMER (*J. Physiol.*, 1906, 34, 93—103).—It is shown that in no circumstances, whatever the diet, does the pancreatic juice in animals contain lactase. The adaptation of the pancreas in secreting lactase, stated to occur in animals fed with milk or with lactose, does not exist. The opposite result previously obtained by Weinland and by Bainbridge was due to fallacious methods of experiment and analysis. This suggests some doubt as to Pawloff's general view regarding the adaptation of the pancreatic secretion to the nature of the foods given.

W. D. H.

Metabolism and Action of Nerve-cells. F. H. SCOTT (*Brain*, 1905, 506—526).—The microchemical reactions of Nissl's granules in nerve-cells indicate their similarity to a substance found in pancreatic and gastric cells. Held's neurosomes are morphologically homologous with the zymogen granules of gland-cells. There is an interdependence between the amount of Nissl substance and the number of neurosomes, exactly as there is between the prozymogen of Macallum and the number of zymogen granules. The nuclei of nerve-cells and gland-cells also resemble one another. All these cells are considered to control changes in proteids, and the hypothesis is advanced that nerve-cells form a proteolytic ferment.

W. D. H.

Influence of Diet on Growth and Nutrition. CHALMERS WATSON and ANDREW HUNTER (*J. Physiol.*, 1906, 34, 111—132).—A detailed account of experiments previously published (this vol., ii, 101).

W. D. H.

Nutrition with Proteid and Glycogen Analysis. EDUARD PFLÜGER (*Pflüger's Archiv*, 1906, 111, 303—308).—The flesh of the cod is at all times almost free from both glycogen and fat. Whether there is more glycogen in the muscles of the living animal is not yet settled. The ash is largely removed by boiling, but this can be again added to the flesh; whether the addition be made or not, a pure cod diet is harmful and provokes diarrhœa, but this may be overcome by mixing it with gelatin. Such a diet is peculiarly suited to experiments on pure proteid nutrition.* The proteid intake can be increased by adding "nutrose" (not nutritin, for that contains 6 per cent. of fat).

Some difficulties experienced in the estimation of glycogen in cod flesh are described.

W. D. H.

Effect of Cerebral Anæmia on Nerve-cells. LEONARD E. HILL and FREDERICK W. MOTT (*Proc. Physiol. Soc.*, 1905—6, iv—v; *J. Physiol.*, 34).—In anæmia produced by ligation of all four cerebral arteries, although the nerve-cells show chromatolysis, swelling, and sometimes displacement of the nucleus, they are not incapable of recovery, because the neuro-fibrils can, by Cajal's method, be shown to remain intact.

W. D. H.

Fatigue of Nerves. F. H. SCOTT (*J. Physiol.*, 1906, 34, 145—162).—The ineffectiveness of a nerve on prolonged stimulation cannot be explained by abolition of conductivity of the nerve-ending. It must be supposed that the nerve-cells secrete something, the passage of which to the ending is necessary for effective stimulation. Recovery after transient fatigue is thus accounted for, but the absence of recovery after prolonged excitation is attributed to the whole of the substance being used up and to their being incapable of obtaining more when severed from their nerve-cells.

W. D. H.

Chemical Stimulation of the Cortex Cerebri. SAMUEL S. MAXWELL (*Univ. Calif. Publ. Physiology*, 1906, 3, 17—19).—Previous observers have stated that the cortex of the brain is inexcitable to chemical, as it is to mechanical, irritation. The chemicals used, however, were not those now known to act as nerve-stimulants. The best for the purpose are those the anions of which precipitate calcium. Accordingly, in the present research, citrates, oxalates, and fluorides were employed, as well as sodium chloride, creatine, and creatinine. Neither as solids nor in solution, however, was any stimulation produced unless the material were applied to the white matter beneath the cortex; this is best done by injecting a few drops with a capillary tube; the response was then immediate, and the results resembled those obtained by the ordinary electrical method. It is suggested that electrical excitation changes the concentration of ions possibly of the calcium precipitants, and that in this method the spreading of the lines of force makes it difficult to say whether it is grey or white matter which is really excited.

W. D. H.

Preparation of Cholesterol from Brain. OTTO ROSENHEIM (*J. Physiol.*, 1906, 34, 104—105).—Water is removed by mixing the

finely-divided brain with plaster of Paris and then extracting with acetone. The first extract contains some water, and therefore less cholesterol. From the second and third extracts, the bulk of the cholesterol crystallises out. On recrystallisation, it shows the melting point and optical activity of the pure substance.

W. D. H.

Cholesterol of Brain. M. CHRISTINE TEBB (*J. Physiol.*, 1906, **34**, 106—110).—Only pure cholesterol is obtainable from the human brain when Rosenheim's method of extraction is employed (see preceding abstract). Cholesterol-ethers were not obtainable, Baumstark's statement to the contrary being due to the imperfections in his method. This conclusion coincides with that Bünz (Abstr., 1905, ii, 841) arrived at by a different method. Mixtures of cholesterol and cholesterol-esters gave melting points lower than that of cholesterol itself, but the extreme depression noted by Bünz was not observed.

W. D. H.

Osmotic Pressure and Heart Activity. A. J. CARLSON (*Amer. J. Physiol.*, 1906, **15**, 357—370).—Details of experiments on the heart of the tortoise and king crab (*Limulus*) are given, which show that hypertonicity depresses, and hypotonicity stimulates. The osmotic changes in the blood is a possible factor in disease.

W. D. H.

Intracellular Colloidal Salts. WILLIAM A. OSBORNE (*J. Physiol.*, 1906, **34**, 84—92).—If a dissociable salt composed of colloidal acid and crystalloid base is dialysed against a solution of a dissociable crystalloid salt, the base of the latter will replace that of the former. As such complex salts exist within cells, it is justifiable to assume that the bases present are those of the lymph which can penetrate the cell wall. The toxic action of pure sodium chloride solution must be in part due to the replacement of the intracellular bases by sodium. If in the colloidal salt the free acids have a low solubility and form a fine suspension when partially precipitated, then total precipitation of the acid will occur when the salt is dialysed against solutions of diffusible weak acids, although such acids have a hydrogen ion concentration too low to effect such change without dialysis. The same result will follow when a salt is dialysed against distilled water, but here the action is slow. This slow loss of base must be taken into account when living cells are exposed to distilled water. Proteid solution dialysed against a weak solution of mercuric chloride tends to retain the heavy metal and thus acquire a greater concentration of the latter than exists in the dialysing fluid. This reaction with heavy metals has an important application with regard to antiseptics and oligo-dynamical action.

W. D. H.

The Liver as a Storehouse for Proteids. WILHELM SEITZ (*Pflüger's Archiv*, 1906, **111**, 309—334).—Observations, partly histological, partly chemical, on starved and fed animals support Pflüger's view that the liver is a storehouse, not only for carbohydrates and fats, but for proteids also.

W. D. H.

Study of the Phosphorus Content of Flesh. A. D. EMMETT and HARRY S. GRINDLEY (*J. Amer. Chem. Soc.*, 1906, **28**, 25—63. Compare Abstr., 1905, ii, 542).—Of the total phosphorus in beef, 75 per cent. is soluble in cold water; one-fourth is present in soluble organic compounds, whilst the relation of soluble organic to soluble inorganic phosphorus is 3:5. The corresponding results for veal are 64 per cent., one-sixth, and 3:9. The percentages of phosphorus in the ash of beef and veal are 17·8 and 12·8. •

The soluble organic phosphorus of flesh is not in combination with the coagulated proteid, albumoses, or peptones. The compounds are not decomposed by a considerable excess of nitric acid.

The Hart-Andrews method (*Amer. Chem. J.*, 1903, **30**, 470) of separating and determining the inorganic and organic phosphorus gives satisfactory results in aqueous extracts freed from coagulable proteids. N. H. J. M.

Distribution of Glycogen in Horse-flesh. RUDOLF HEFELMANN and PAUL MAUZ (*Zeit. öffentl. Chem.*, 1906, **12**, 61—63).—The following quantities of glycogen were obtained from the various muscles of slaughtered horses, the figures expressing percentages on the dry, fat-free flesh:

	Lean Harness Horse.	Well-nourished. Horse.
Facial muscles.....	0·24	0·047
Leg muscles.....	1·80	7·97
Back muscles	2·87	10·80
Abdominal muscles...	3·92	10·15
Flank muscles.....	4·22	10·51

W. P. S.

Filtration in the Living Organism. LEONARD E. HILL (*Biochem. J.*, 1906, **1**, 55—61).—A discussion of the part filtration plays in physiological phenomena, the underlying idea of which is that, as in liquids and colloidal solutions (for example, in living cells) the pressure is equally transmitted in all directions, filtration can play little or no part in such phenomena as lymph-production and secretion.

W. D. H.

The Stimulus to Milk Secretion. WALTER HEAPE (*Proc. Physiol. Soc.*, 1905—6, i—ii; *J. Physiol.*, **34**)—Starling's view, that the hormone in milk secretion is an internal secretion from the fœtus, is disputed, for the mammary glands may be active in virgin animals. The source of the stimulus is regarded as the ovary, which forms a hypothetical material named "gonadin."

NOTE BY ABTRACTOR.—In the discussion which ensued, Starling pointed out that the difference between the ovarian ovum and the more elaborate ovum called a fœtus is one of degree only. W. D. H.

Composition of Colostrum. ERNST WINTERSTEIN and E. STRICKLER (*Zeit. physiol. Chem.*, 1906, **47**, 58—82).—The colostrum proteid, which is heat-coagulable, yields, on hydrolysis, alanine, amino-

valeric acid, leucine, pyrrolidine-2-carboxylic acid, serine, phenyl-alanine, tyrosine, aspartic acid, glutamic acid, cystine, arginine, histidine, lysine, tryptophan, ammonia, and other substances not identified. It also contains one or more carbohydrate complexes. Cow's colostrum contains caseinogen, albumin, globulin, fat, free fatty acids, lecithin, cholesterol, free glycerophosphoric acid, lactose, and urea. Tyrosine, choline, nuclein, and hexone bases were not found. Besides lactose, there is no optically active reducing carbohydrate. Quantitative results are given. W. D. H.

The Baudouin Reaction in the Fat of Human Milk. RODOLPHE C. ENGEL (*Zeit. angew. Chem.*, 1906, 19, 283—286. Compare Abstr., 1905, ii, 468).—After ingestion of sesame oil, the fat of human milk gives the Baudouin reaction. The reaction is obtainable from one to one and a half hours after partaking of the oil and before the iodine number of the oil increases. L. DE K.

Free Amino-acids in Urine. GUNNAR FORSSNER (*Zeit. physiol. Chem.*, 1906, 47, 15—24).—Ignatowski's naphthalene- β -sulphonic chloride method was employed for the isolation of amino-acids in urine. The point investigated was whether the excretion of amino-acids can be used in the differential diagnosis of gout. The conclusion reached is that free glycine often occurs in the urine of normal persons and in those suffering from a variety of diseases, gout included. W. D. H.

Salt Glycosuria. FRANK P. UNDERHILL and OLIVER E. CLOSSON (*Amer. J. Physiol.*, 1906, 15, 321—332).—A full account of experiments previously published (this vol., ii, 186). W. D. H.

Action of Acids and Alkalis and of Acid, Neutral, and Alkaline Salts on Tadpoles. HERBERT E. ROAF (*Bio-chem. J.*, 1906, 1, 88—110).—The ions which exert the most powerful action on tadpoles are those of hydrogen and hydroxyl, which kill in concentrations of 0.001 and 0.002*M.* respectively. These ions probably form more stable compounds or aggregations with protoplasm than do those of neutral salts. The degree of toxicity of acid and alkaline salts is roughly proportional to the concentration of hydrogen or hydroxyl ions in their solutions. Neutral salts do not kill until the osmotic pressure rises above that of the fluids of the organism. There is, therefore, a long range where such salts are comparatively harmless, above which is a short range where they are rapidly fatal. Unchanged volume of living cells does not necessarily imply isotony. Some normal salts, however, like those of heavy metals, barium, and ammonium, have specific poisonous effects. Some ions, in concentrations below the lethal, accelerate growth; this is most pronounced with phosphates. W. D. H.

Pharmacological Action of Digitalis, Strophanthus, and Squill on the Heart. G. S. HAYNES (*Bio-chem. J.*, 1906, 1, 62—87).—The experiments were carried out on the isolated mammalian heart. It is essential that drugs such as those used should be standardised by

bio-chemical methods. The toxicities of tincture of digitalis and squill are equal, that of strophanthus is nine or ten times as great. Two stages in the action on the heart are noticed: (1) stimulation of the cardiac muscle and vagal nerve endings; (2) increase of tonus and acceleration. In therapeutical doses, squill increases the force of the heart much more than the other two drugs; it slows the heart more, and causes more constriction of the coronary vessels. Digitalis is the least efficient of the three. After atropinisation, the drugs cause very little decrease in the heart's rate. Digitalis is most irritant to mucous membranes, then comes squill, whilst strophanthus has very little irritant action. Squill should be used in preference to the others to raise blood-pressure.

W. D. H.

Pharmacological Studies of Magnesium Salts. II. The Toxic Action of Intravenous Injections on the Medullary Centres. SAMUEL J. MELTZER and JOHN AUER (*Amer. J. Physiol.*, 1906, 15, 387—405. Compare Abstr., 1905, ii, 743).—Intravenously injected magnesium salts are very toxic, but if the injection is made slowly the effects are not much shown, hence the apparent harmlessness of magnesium sulphate given by the mouth in man. The most marked effects are on the respiratory centre. It is completely inhibited, is irresponsive to venous blood, and the reflex effect of sensory stimuli is reduced. Prolonged artificial respiration produces restoration. *There is a similar but less marked effect on the deglutition centre, and a still less marked effect on the vaso-motor centre.

W. D. H.

Proportion of Chloroform in the Organism during Anæsthesia. J. TISSOT (*Compt. rend.*, 1906, 142, 234—237).—In animals rapidly anæsthetised by chloroform, the amount present in the blood may exceed 50 mg. per 100 c.c., and may reach 70—80 mg. If the anæsthesia is slowly induced it sinks to 45 or even 35 mg. More than 70 mg. per 100 c.c. of arterial blood often causes death. In the brain the chloroform is in equilibrium with that in the blood. If a fatal result ensues at the moment of the heart's arrest, the amount in the blood is more than in the brain, but afterwards the amount in the brain is often higher than that in the venous blood. The amount in venous blood is always less than in arterial blood. The length of the period of anæsthesia, proportion of chloroform in the brain, and rapidity of blood circulation are important factors.

W. D. H.

Behaviour of Nitrobenzene and other Aromatic Nitro-compounds in the Organism. ERICH MEYER (*Zeit. physiol. Chem.*, 1905, 46, 497—509).—Nitrobenzene administered either *per os* or subcutaneously is converted into *p*-nitrophenol and this into *p*-aminophenol. Aniline is also converted into *p*-aminophenol. *m*-Nitrophenol is partly transformed into *m*-aminophenol.

E. F. A.

Action of Hordenine Sulphate on the Circulation. LUCIEN CAMUS (*Compt. rend.*, 1906, 142, 237—239).—**Action of Hordenine Sulphate, Soluble Ferments, and Microbes** (*ibid.*, 350—352).—Hordenine sulphate is hæmolytic, and retards the coagulation of the

blood. A small dose excites the vagus nerve and slows the heart, a large dose has the opposite effect. It hinders the action of pepsin, trypsin, and rennin, but the antagonism is indirect, depending on the amount ; if the ferment action is stopped, it goes on again by increasing the proportion of ferment. The ferment is not destroyed, only rendered latent. Invertin, maltase, and lipaseidin are not arrested. Its antiseptic action is mainly due to the alterations in osmotic pressure it produces. Clinically the drug has proved valuable. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Germicidal Action of Potassium Permanganate. JAMES B. GARNER and WALTER E. KING (*Amer. Chem. J.*, 1906, 35, 144—147).—A series of experiments has been made on the action of potassium permanganate solutions of various concentrations on a pure bouillon culture of *Bacillus typhosus* at a temperature of 37.4°. The results show that N/511 potassium permanganate is antiseptic and that N/458 solution is germicidal to the organism. E. G.

Study of the Process of Nitrification with Reference to the Purification of Sewage. HARRIETTE CHICK (*Proc. Roy. Soc.*, 1906, B, 77, 241—266).—Nitrification in the purification of sewage, notwithstanding the large amount of organic matter present, is attributed to (1) the presence of organisms in symbiosis with nitrifying organisms, by which the latter are rendered more resistant; (2) the retention of most of the organic matter near the surface of the filters; and (3) to the very large numbers of nitrifying organisms present in the filters (compare Winogradsky and Omelianski, *Centr. Bakt. Par.*, 1899, ii, 5).

Production of nitrites and nitrates may occur together, or the second process may be retarded when the sewage is strongly ammoniacal.

No evidence was obtained that absorption of ammonia or ammonium salts ever occurs. Nitrification is extremely rapid, being completed during the time required by percolation (2—3 hours).

Of the two processes investigated, continuous filters and contact beds, the former was found to be the more effective and possesses the further advantage that clogging is more easily remedied than in the case of contact beds. N. H. J. M.

Amide Nutrition of Green Plants in Absence of Carbon Dioxide. JULES LEFÈVRE (*Compt. rend.*, 1906, 142, 287—289).—In absence of both amides and carbon dioxide (the carbon dioxide liberated being absorbed by baryta), the plants lost in weight. Similar plants

provided with amides developed in absence of carbon dioxide. When, however, these plants were kept for a time in darkness there was no further growth.

N. H. J. M.

Variations in Phosphoric Acid and Nitrogen in the Leaf Sap of Certain Plants. GUSTAVE ANDRÉ (*Compt. rend.*, 1906, 142, 226—227).—In annual plants, a portion of the phosphoric acid migrates from the leaf to the ovule as soluble mineral phosphate, whilst another portion is displaced in combination with nitrogenous substances.

N. H. J. M.

Insoluble Alkali Compounds in Living Plants: Oak Leaves. MARCELLIN BERTHELOT (*Compt. rend.*, 1906, 142, 249—257).—Fresh oak leaves, when treated with calcium hydroxide, did not give off ammonia. When distilled with water, a trace of a substance which reduced ammoniacal silver nitrate was obtained, but no furfuraldehyde. The amounts of ash constituents, soluble and insoluble in cold water, were found to be as follows (per cent. of organic matter):

	Na ₂ O.	K ₂ O.	CaO.	MgO.	SiO ₂ .
Soluble.....	0.17	6.0	2.3	1.05	0.9
Insoluble	trace	0.17	1.40	0.30	1.47

Maceration with potassium acetate slightly increased the insoluble potassium and the soluble calcium and magnesium. Sodium acetate rendered a small amount of the sodium insoluble. With calcium acetate a distinct amount of the calcium became insoluble, whilst the potassium and magnesium were partially dissolved. Magnesium acetate had a similar effect, the insoluble magnesium and the soluble potassium and calcium being increased.

When the dried leaves were extracted successively with water and dilute hydrochloric acid, a small amount of calcium and traces of magnesium remained undissolved, but no potassium. The residue was well washed, dried, and treated with potassium acetate. This treatment resulted in the fixation, by the organic matter, of a considerable proportion of the potassium, whilst at the same time some of the calcium dissolved.

N. H. J. M.

Insoluble Potassium Compounds in the Trunk and Bark of Oaks. MARCELLIN BERTHELOT (*Compt. rend.*, 1906, 148, 313—316).—The acid, which forms insoluble compounds of potassium, exists only in traces, if present at all, in the trunk of oaks. The insoluble compounds of potassium and the acids which produce them are mainly in the leaves.

N. H. J. M.

New Method of Extracting Star Aniseed Oil. PH. EBERHARDT (*Compt. rend.*, 1906, 142, 407—408).—The usual source of this oil, whether extracted from *Illicium anisatum* or *Illicium verum*, is the fruit. The author's experiments show that it may be advantageously obtained by distillation of the leaves, and by this mode of operating the annual production should be greatly increased.

H. M. D.

"Denji" and "Nzonogwi" Fibres from British Central Africa (*Bull. Imp. Inst.*, 1905, 3, 23—25).—A sample of "Denji" fibre, obtained from the bark of *Sida rhombifolia*, when examined by the methods of Cross and Bevan (*Report on Indian Fibres exhibited at the Indian and Colonial Exhibition*, 1886) gave the following results: moisture, 10·3 per cent.; ash, 1·0 per cent.; loss on α -hydrolysis, 8·5 per cent.; loss on β -hydrolysis, 13·5 per cent.; loss on mercerisation, 7·5 per cent.; loss on acid purification, 1·8 per cent.; gain on nitration, 23·6 per cent.; cellulose, 77·4 per cent. A specimen of "Nzonogwi" fibre, from the bark of *Triumfetta rhomboidea*, gave the following results: moisture, 10·4 per cent.; ash, 0·6 per cent.; loss on α -hydrolysis, 9·1 per cent.; loss on β -hydrolysis, 14·7 per cent.; loss on mercerisation, 8·5 per cent.; loss on acid purification, 3·4 per cent.; gain on nitration, 30·2 per cent.; cellulose, 76·2 per cent. Both these fibres resemble jute in chemical characters and composition.

E. G.

[Constituents of] the Seeds of the Para Rubber Tree (*Hevea brasiliensis*) (*Bull. Imp. Inst.*, 1903, 1, 156—159).—An account is given of the investigation of the constituents of a sample of the seeds of the Para rubber tree (*Hevea brasiliensis*) obtained from the Federated Malay States.

The kernels constitute about 50 per cent. of the whole seeds, and contain 42·3 per cent. of oil, whilst the whole seeds (husks and kernels together) yield 20 per cent. of oil. The oil obtained from the kernels by extraction with light petroleum is clear, light yellow, and has an odour resembling that of linseed oil; it belongs to the class of drying oils and, on exposure to the air, yields a clear, transparent film. The husks contain a small quantity of a solid fat which has a high saponification number and a low iodine value. The oil from the kernels gave the following constants: sp. gr. at 15°, 0·9302; acid number, 10·7; free fatty acids (calculated as oleic acid), 5·4 per cent.; ester number, 195·4; saponification number, 206·1; iodine number, 128·3. The constants of the oil extracted from the whole seeds were as follows: sp. gr. at 15°, 0·9316; acid number, 19·0; free fatty acids (calculated as oleic acid), 9·6 per cent.; ester number, 90·4; saponification number, 209·3; iodine number, 121·2.

A sample of the meal of the seeds which had been ground in the Federated Malay States yielded 36·1 per cent. of an oil which had a slightly acid odour, and, when left, solidified as a soft, crystalline, yellow mass; this product began to melt at 19°, was a clear liquid at 28°, and furnished the following constants: sp. gr. at 15°, 0·911; acid number, 130·5; free fatty acids (calculated as oleic acid), 65·6 per cent.; ester number, 65·2; saponification number, 195·7; iodine number, 136·2. It was found that the large amount of free acids in this oil was due to decomposition brought about by the action of a hydrolytic enzyme contained in the seed.

The meal was found to have the following composition: moisture, 9·1 per cent.; ash, 3·53 per cent.; fibre, 3·4 per cent.; oil, 36·1 per cent.; proteids, 18·2 per cent.; carbohydrates, 29·67 per cent. The ash contained 30·3 per cent. of phosphoric acid (calculated as P_2O_5).

The results of the investigation indicate that the oil of the seeds of *Hevea brasiliensis* could probably be employed for the purposes to which linseed oil is applied, whilst the residual cake would be of value as a cattle food. E. G.

Occurrence of Quebrachitol in the Latex of *Hevea brasiliensis*. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1906, **25**, 48—49).—When the latex is coagulated in alcohol and the alcoholic solution so produced is evaporated, it deposits crystals of quebrachitol. This melts at 190—191°, has $[\alpha]_D - 80.2^\circ$ in water, and is converted by hydriodic acid into *l*-inositol, which melts at 236° and has $[\alpha]_D - 65.0^\circ$ in water (compare Tanret, *Abstr.*, 1890, 226). T. A. H.

Cinchona Barks and their Cultivation. DAVID HOWARD (*J. Soc. Chem. Ind.*, 1906, **25**, 97—99).—An historical account of the methods of cultivation and hybridisation employed in India and Java for increasing the yield of alkaloid in various species of cinchona plant. By careful selection in Java the amount of "quinine alkaloid" in the bark has been raised from 4 to 10 per cent. P. H.

Comparative Values of Different Grades of Wheat of Crops of 1903 and 1904. R. HARCOURT (*J. Amer. Chem. Soc.*, 1906, **28**, 66—73).—The milling, chemical, and baking tests failed to show any wide differences in the products of the wheats studied. The products of the lower grades are inferior in yield of flour and in the colour of the bread, but there was little or no difference in strength and in yield of bread. N. H. J. M.

Nutritive Value of the Non-proteid Nitrogen Compounds in Foods. ERNST SCHULZE (*J. Landw.*, 1906, **54**, 65—81).—Potatoes and malt germs contain relatively large amounts of asparagine; man-golds generally contain small amounts of glutamine (0.5 to 0.9 gram per litre of juice). Both substances are readily decomposed when consumed by animals, being probably converted first into the corresponding amino-acids and afterwards into succinic or malic acid, which can have no value for fat production. Other amides, however, contain relatively much less carbon in the form of carboxyl and have probably considerable nutritive value.

The fact that asparagine is of no use in the case of carnivorous animals, whilst it economises proteids in the case of ruminants, may be due to the action of microbes on asparagine; the asparagine may be decomposed by the microbes and the products resorbed by the ruminant, or it may be utilised for producing proteids to be afterwards digested.

Strusiewicz (*Inaug. Diss. Göttingen*) considers that the amides in sugar-beet molasses are equal to proteids, and should therefore not be deducted from the digestible proteids. N. H. J. M.

Constituents of Emmenthaler Cheese. III. ERNST WINTERSTEIN and W. BISSEGER (*Zeit. physiol. Chem.*, 1906, **47**, 28—57. Compare *Abstr.*, 1904, ii, 585).—The analyses deal with the nitrogen

and the way in which it is distributed between proteids (coagulable and peptone-like), bases, ammonia, amino-acids, &c., in cheeses of different ages.

W. D. H.

Example of how Analysis of Soil may be of use. ADOLF MAYER (*J. Landw.*, 1906, 54, 47—50).—Analyses of four tobacco soils from Deli (Sumatra) showed that three of them, which yield satisfactory crops, contained 0·14 to 0·16 per cent. of potash soluble in dilute hydrochloric acid, whilst one soil, known to require potassium manure, was found to contain only 0·05 per cent. of potash.

The loss on ignition corresponds approximately with the amount of humus (determined by the chromic acid method) only in the case of sandy soils and sandy peat soils. The heavy loamy soil at Wageningen, which contains only 0·8 per cent. of humus, loses 4 to 5 per cent. when ignited.

N. H. J. M.

Absorption of Alkali Carbonates by the Mineral Constituents of the Soil. J. DUMONT (*Compt. rend.*, 1906, 142, 345—347).—The sandy constituents of soils mechanically separated have no action on alkali carbonates, and kaolin acts very feebly. Silica, even when dried, decomposes cold solutions of potassium carbonate, but in a less degree than other colloids. Iron and aluminium hydroxides act very energetically, the latter being comparable with clay. The more vigorous action of clay as compared with that of its components whether separate or together is difficult to explain.

LÉON MAQUENNE (*ibid.*, 347) points out that the behaviour of clay accords with what its constitution would indicate. In consequence of the position of its OH groups, clay is able to form, both with bases and with acids, compounds probably dissociable by water.

N. H. J. M.

Chemical Study of Some Oregon Beaverdam Soils. C. E. BRADLEY (*J. Amer. Chem. Soc.*, 1906, 28, 64—65).—The soils consist largely of decayed leaves, twigs, and larger pieces of wood with more or less clay, and the name is derived from the fact that the swamps were formed by the streams being dammed by beavers. Analyses of five samples of the soils (one virgin and four farmed) gave the following results: silica, 20·43—53·05; loss on ignition, 31·5—63·95; Na_2O , 0·16—0·43; K_2O , 0·10—0·28; CaO , 0·26—1·18; MgO , 0·06—0·33; Fe_2O_3 , 4·00—9·21; Al_2O_3 , 4·95—8·07; P_2O_5 , 0·21—2·30; SO_3 , 0·08—0·23; N, 0·78—2·06. One of the soils has grown fifty good crops of onions without manure. The potassium is of low availability, whilst the phosphoric acid is largely available.

N. H. J. M.

Analytical Chemistry.

Estimation of Halogens in Organic Compounds. WILHELM VAUBEL and OTTO SCHEUER (*Chem. Zeit.*, 1906, **30**, 167—168).—The apparatus consists of a Wurtz flask fitted with a stoppered separating funnel. The side-tube is connected to a Volhard bulb apparatus containing a solution of silver nitrate. About 0.5 gram of the substance is put into the flask and about 50 c.c. of sulphuric acid are introduced from the funnel. In order to generate a slight excess of sulphurous acid it is best to add to the mixture a little filter paper or some metallic copper. On heating, the halogen is expelled and the last traces are removed by means of a current of air. The halogen silver precipitate is freed from co-precipitated silver sulphite by boiling with dilute nitric acid, collected and weighed.

Very good results may be obtained with various halogenated compounds, provided they are not too volatile. L. DE K.

[**Estimation of Chlorine Peroxide.**] WILLIAM BRAY (*Zeit. physikal. Chem.*, 1906, **54**, 569—608. See this vol., ii, 223).

Detection of Ozone by means of Silver. HERMANN THIELE (*Zeit. öffentl. Chem.*, 1906, **12**, 11—12).—The author has observed that silver foil or money which has been polished with sand between the fingers or handled to any extent is no longer blackened when exposed to an atmosphere containing ozone. When, however, the silver has been momentarily heated in a flame or has been polished with emery paper, it is at once blackened by the presence of ozone. If the trace of fatty matter derived from the fingers is the cause of the non-appearance of the black colour, it is curious that so extremely minute a trace of fat as must be present should prohibit the reaction, seeing that a layer of india-rubber several millimetres in thickness is at once penetrated by ozone. W. P. S.

Estimation of Phosphoric Acid in Manures as Phosphomolybdic Anhydride. GEORG BERJU (*J. Landw.*, 1906, **54**, 31—46).—Neumann's method (*Abstr.*, 1898, ii, 454) gives very exact results, and is not influenced by the nature of the solvent or by the presence of dissolved silicic acid. In the case of high per cent. phosphates it is desirable to precipitate with about 100 c.c. of the molybdate solution, employing about 0.25 gram of substance.

Methods in which the phosphoric acid was directly precipitated as magnesium ammonium phosphate gave too high results.

N. H. J. M.

Removal of Arsenic from Hydrochloric Acid for Use in the Marsh-Berzelius Method. ARTHUR R. LING and THEODORE RENDLE (*Analyst*, 1906, **31**, 37—38).—To 1500 c.c. of commercial hydrochloric acid of sp. gr. 1.1 about 40 c.c. of re-distilled commercial wood-spirit are added together with 5—10 grams of arsenic-free granulated zinc.

The mixture is contained in a Wurtz flask, which is connected with a reflux condenser by means of an ordinary cork. A glass rod is fixed in the cork and carries a coil of electrolytic copper foil, having a surface of about 120 sq. inches. After plugging the side-tube of the flask, the condenser is connected with an exhaust-pump and the mixture boiled for about three hours, the copper being withdrawn and cleansed at least once during this period. Two flasks should be interposed between the condenser and the pump: the first acts as a receiver for a tarry liquid which distills over, whilst the second contains water to absorb any hydrogen chloride passing over. The mixture is then distilled over electrolytic copper foil.

W. P. S.

Reactions and Estimation of Arsenic Hydride. HANS RECKLEBEN and GEORG LOCKEMANN (*Zeit. angew. Chem.*, 1906, 19, 275—283).—In estimating arsenic hydride in a mixture of gases, the best absorbent, and the most suitable for determining its volume from the loss, is a solution of sodium hypochlorite (commercial "Eau de Javelle").

For detecting the presence of arsenic hydride, a strong ammoniacal solution of silver nitrate is the best test; it gives at once a dark deposit. The test is obviously not available in presence of other gases (phosphine, stibine, hydrogen sulphide, &c.), which give dark precipitates with silver nitrate, but the absence of any reaction is a certain proof of the absence of arsenic hydride.

L. DE K.

Detection of Boric Acid. GEORG FENDLER (*Zeit. Nahr. Genussm.*, 1906, 11, 137—144).—It is shown that boric acid may be estimated approximately in solutions by dipping strips of turmeric paper into them and noting the time required for the appearance of a red coloration when the strips are removed and allowed to dry. Comparative solutions containing known amounts of boric acid must be employed. Attention is also drawn to the fact that traces of boric acid are often present in hydrochloric, sulphuric, and acetic acids.

W. P. S.

Some Difficulties in the Estimation of Carbon Monoxide in Gaseous Mixtures. ARMAND GAUTIER and PAUL CLAUSMANN (*Compt. rend.*, 1906, 142, 485—491. Compare Abstr., 1898, ii, 535, 537, 640; 1899, ii, 451).—Analysis of a number of gaseous mixtures containing carbon monoxide and hydrogen with or without air has shown that the absorption of carbon monoxide by an acid solution of cuprous chloride is never complete, neither is the residual carbon monoxide completely burnt in the eudiometer when the gaseous mixture is exploded with excess of oxygen; the amount of carbon monoxide that escapes detection, varying from 1 to 0.3 per cent., is greatest in those mixtures which contain the least quantity of the gas, and it can be estimated by means of iodine pentoxide (compare Abstr., 1898, ii, 537).

M. A. W.

Method for Determining "Black Alkali" in Irrigating Waters and Soil Extracts. W. W. SKINNER (*J. Amer. Chem. Soc.*, 1906, 28, 77—80).—The water or extract (200 c.c.) is mixed

with *N*/50 sodium carbonate (50 to 150 c.c.) and evaporated to dryness in a platinum or silver dish. The residue is rubbed with distilled water free from carbon dioxide, transferred to a 100 c.c. flask, which is then filled to the mark, and well shaken. After twelve to fifteen hours, 50 c.c. of the clear solution are titrated with *N*/50 sulphuric acid in presence of chloroform (5 c.c.) and 0.025 per cent. erythrosin (1 c.c.). The solution is vigorously shaken after each addition of acid.

When less sulphuric acid is required than is necessary to neutralise one-half of the sodium carbonate, some of the sodium carbonate has reacted with soluble calcium and magnesium salts, indicating that no excess of "black alkali" was present, but rather an excess of permanent hardness. The difference in c.c. between the sulphuric acid required and one-half of the sodium carbonate is multiplied by 0.00136, which gives the equivalent of calcium sulphate in 100 c.c.

When more sulphuric acid is required than is equivalent to one-half the sodium carbonate, "black alkali" is present, and the difference in c.c. multiplied by 0.00106 gives the amount of it in terms of sodium carbonate.

"Black alkali" may consist of carbonates and acid carbonates of any of the alkalis. Only the alkalinity due to the carbonates and bicarbonates of the alkalis and not those of the alkaline earths should be expressed as black alkali.

N. H. J. M.

Estimation of Opalescent Silver Chloride Precipitates.
ROGER C. WELLS (*Amer. Chem. J.*, 1906, **35**, 99—114. Compare Richards and Wells, *Abstr.*, 1904, ii, 287).—A study has been made of the variation of opalescence with time, ground glass being employed for standards of reference. The results of the experiments show that the medium is the most important variable in nephelometric observations. Determinations have been made of the maximum opalescences which could be obtained in various media, and the excess of soluble chloride and length of time required to produce them. In order to obtain maximum opalescence, it is found that for every concentration a suitable medium and excess of the precipitant are required. The substances which aid in producing maximum opalescence also hasten the speed of its formation. Electrolytes, such as salts and mineral acids, are found to produce the greatest acceleration. Attention is drawn to the bearing of the results on the theory of colloidal solution and on certain photographic changes. The chief sources of error in nephelometric work are discussed, and precautions are suggested for several typical cases.

E. G.

Estimation of Mercury and Iodine in Antiseptic Soaps.
ATHERTON SEIDELL (*J. Amer. Chem. Soc.*, 1906, **28**, 73—77).—About 10 grams of the sample are dissolved in 150 c.c. of strong alcohol, and, after acidifying with a few c.c. of hydrochloric acid, the mercury is precipitated as sulphide by a current of hydrogen sulphide, collected on a Gooch filter, washed with alcohol, and weighed. The filtrate is concentrated to about one-half and, after making up to the original volume with water, the separated fatty acids are removed

by filtration. After adding 25—50 c.c. of chloroform, the iodine is liberated by cautious addition of nitrous acid and the whole is well shaken. The iodine dissolved in the chloroform is then titrated in the usual manner with standard thiosulphate solution. L. DE K.

Variable Sensitiveness in the Colorimetry of Chromium. DAVID W. HORN (*Amer. Chem. J.*, 1906, 35, 253—258).—A series of experiments has been made with the object of determining the concentration at which the colour of potassium chromate is most sensitive to change on diluting the solution. The results show that both the sensitiveness and the ease of determination vary with the concentration, but that there is no simple general relation between the sensitiveness and the concentration. The sensitiveness is found to be greatest at concentrations between 0.004*N* and 0.008*N* with respect to the gram-atom of chromium. Colorimetric comparisons have also been made with green chromium chloride solutions, and it is found that, in general, the sensitiveness is similar to that of potassium chromate solutions. E. G.

Rapid Electrolytic Precipitation of Antimony. JULIA LANGNESS and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1905, 27, 1524—1527).—Ten c.c. of the solution containing not more than 0.24 gram of the metal are mixed with 15 c.c. of solution of sodium sulphide of sp. gr. 1.18, 3 grams of potassium cyanide, 1 c.c. of 10 per cent. sodium hydroxide, and water up to 70 c.c. After heating nearly to boiling, the solution is electrolysed with a current of 3.5—4 volts and 6 amperes, the time being fifteen minutes. Roughened dishes should be used as cathodes.

Very satisfactory results are obtained in the presence of arsenic under the following conditions: 10 c.c. of solution, 15 c.c. of sodium sulphide, 3 grams of potassium cyanide, and water up to 70 c.c. In fifteen minutes, the antimony is completely precipitated when using the rotating anode and a current of 6 amperes and 4 volts.

The process may be used in the assay of the mineral stibnite, 0.5 gram of which may be at once dissolved in 20 c.c. of sodium sulphide and treated as directed. L. DE K.

Wine Analysis. Estimation of "Added" Water, Alcohol, or Sugar. Determination of Sugar in "Incompletely Fermented" and "Liqueur" Wines. MAXIME CARI-MANTRAND (*Bull. Soc. chim.*, 1906, [iii], 35, 174—181, 181—187).—The author states that wine is frequently sophisticated by being diluted with water and suitable additions to the liquid made in order to conform to the minimum legal standard as regards "dry extract," "alcohol content," &c. The following systematic method of analysis is recommended to meet cases of this kind. "Total acidity" is determined by titrating 10 c.c. of the wine with *N*/10 sodium hydroxide, using litmus paper as an indicator in the case of white wine, and the change of tint from the natural red to "absinthe green" as an indication of neutrality in the case of red wine. "Volatile acid" is estimated either by distilling 20 c.c. from a mixture of 10 c.c. of wine with 20 c.c. of water,

or by steam-distilling 50 c.c. of wine and collecting the first 200 c.c. of distillate. In either case the distillate is titrated with *N*/10 soda solution, using phenolphthalein as indicator. By the first method 10/11ths of the total volatile acid is obtained, and a correction for the residue must be made. Very acid wines are frequently partially neutralised. For the estimation of "volatile acid" in such cases 20 c.c. of *N*/10 sulphuric acid is added to 10 c.c. of the wine, which is then distilled and the distillate titrated as described above. The difference in the two results gives the "combined volatile acid."

"Total sulphurous acid" is estimated by adding 25 c.c. of a solution of potassium hydroxide (1 gram-mol. per litre) to 50 c.c. of wine. This mixture is left for fifteen minutes and then 10 c.c. of sulphuric acid, diluted with 30 c.c. of water, is added and the liquid titrated with standard iodine solution, starch being used as an indicator. "Free sulphurous acid" is determined by adding to 50 c.c. of wine 5 c.c. of sulphuric acid, diluted with 15 c.c. of water, and titrating as before. "Potassium bitartrate" is determined by evaporating 100 c.c. of wine to from 7 to 8 grams, filtering out the crystals which have separated after twenty-four hours, washing four times with 5 c.c. of alcohol (42°), dissolving in boiling water, and titrating with *N*/10 soda in presence of phenolphthalein. For "plastered wines" this process is modified, 100 c.c. of wine being evaporated to 10 c.c. and the residue mixed with 25 c.c. of alcohol (42°) and set aside for twenty-four hours. The precipitate obtained is washed, dissolved in boiling water, and the solution titrated as already indicated.

"Free tartaric acid" is estimated by adding 2 c.c. of acetic acid, 5 drops of a 20 per cent. solution of potassium acetate, and 15 grams of potassium chloride to 100 c.c. of wine. When solution is complete, 15 c.c. of alcohol are added, the mixture stirred, and the sides of the vessel rubbed with a glass rod to facilitate the separation of potassium hydrogen tartrate. After twelve hours, the precipitate is collected, washed, dissolved, and titrated as before. The difference between this result and the "potassium bitartrate" previously determined is the equivalent of the free tartaric acid originally present.

Denigés' method for the determination of citric acid is recommended (Abstr., 1902, ii, 365). For the estimation of glycerol, potassium sulphate, and "reducing sugar" the methods in general use are suitable. The ash is determined by igniting, at a red heat, the "dry extract" from 25 c.c. of wine. The character, amount, and alkalinity of the ash afford useful indications as to whether the wine is diseased or whether an alkali has been added to it.

In examining "incompletely fermented" or "liqueur" wines or grape musts to which alcohol has been added, the foregoing factors are frequently of little value and the determination of the amount and nature of the "crystallisable" and "uncrystallisable" sugars present is recommended. For this purpose a convenient quantity of the liquid is decolorised by adding lead subacetate, filtering, and diluting the filtrate to one litre. The quantity required to completely reduce 10 c.c. of Fehling's solution and the optical activity of this liquid are then determined. If "crystallisable" sugar is present, a similar quantity of the original wine is "inverted" by boiling with 2 c.c. of hydro-

chloric acid, decolorised and diluted as before, and the reducing power and optical activity are again determined. These operations are conducted at the same time on a normal grape must (directions for the preparation of which are given in the original) and comparison of the two sets of results obtained is usually sufficient to indicate the nature of the material under examination.

T. A. H.

Volumetric Determination of Organic Hydrosulphides and Thio-acids. PETER KLASON and TOR CARLSON (*Ber.*, 1906, 39, 738—742).—Interaction between hydrosulphides and iodine proceeds under certain conditions quantitatively in accordance with the equation $2R\cdot SH + I_2 = R_2S_2 + 2HI$. The addition of sodium hydrogen carbonate to remove the hydriodic acid formed is not only unnecessary but detrimental. Aromatic hydrosulphides are such strong acids that they form normal salts with alkalis in alcoholic solution and can, accordingly, be titrated with phenolphthalein as indicator. The estimations described were conducted with thio-*p*-cresol, thio- β -naphthol, and methyl, ethyl and isobutyl mercaptans, whilst thioglycollic acid and thioacetic acid also gave satisfactory results.

A. McK.

Fehling's Test for Dextrose in Urine. HUGH MACLEAN (*Biochem. J.*, 1906, 1, 111—122).—Sugar in urine is not so easily detected by Fehling's solution as in water. The masking factor is creatinine, not ammonia, as Pavy suggested; creatine acts in the same way. Creatinine also prevents uric acid from reacting with Fehling's solution.

W. D. H.

Can Sugar be Detected with Certainty in the Urine by the Fermentation Test? EDUARD PFLÜGER (*Pflüger's Archiv*, 1906, 111, 241—250).—Polemical against E. Salkowski. The question in the title is here answered in the negative.

W. D. H.

Estimation of Sugar in Coloured and Decolorised Solutions and the Estimation of Lævulose and Dextrose. A. KICKTON (*Zeit. Nahr. Genussm.*, 1906, 11, 65—72).—The results given show that the colouring matters in wines have but little influence on the estimation of sugar in wine by Fehling's gravimetric method if the precipitated cuprous oxide is converted into cupric oxide before weighing. Practically the same results are obtained whether the sugar is estimated directly in the wine or after the latter has been decolorised by either lead acetate or animal charcoal.

Halenke and Möslinger's formula (*Abstr.*, 1895, ii, 463) as modified by Fresenius is shown to give trustworthy results in cases where lævulose and dextrose are present in about equal quantities, whilst the different reducing powers of the two sugars cause slight discrepancies should one sugar predominate considerably over the other.

W. P. S.

Estimation of Chloral Hydrate. THOMAS E. WALLIS (*Pharm. J.*, 1906, 76, 162—163).—After several trials, the following method is recommended: 0.1 gram of the sample is dissolved in 10 c.c. of

absolute alcohol and mixed in a suitable bottle with 10 c.c. of *N*-sodium hydroxide. The bottle is closed with an india-rubber cork, which is securely tied down, and then heated in the water-bath for three hours. The resulting liquid is neutralised with *N*-sulphuric acid, using phenolphthalein as indicator, and the solution is then titrated as usual with *N*/10 silver nitrate. The chlorine thus found represents the chloral actually present.

L. DE K.

New Method for the Estimation of Acetone. SAMUEL M. AULD (*J. Soc. Chem. Ind.*, 1906, 25, 100—101).—A known quantity of the solution, containing about 0.1 to 0.2 gram of acetone, is placed in a round-bottomed flask of 500 c.c. capacity, diluted with a little water, and mixed with 20 to 30 c.c. of a 10 per cent. solution of potassium hydroxide. The flask, provided with a reflux condenser, is fitted with a dropping funnel, from which a solution of bromine, containing 200 grams of bromine and 250 grams of potassium bromide per litre, is slowly added until the solution assumes a permanent, faint yellow colour. The flask is then heated at 70° for half an hour over a water-bath. It is imperative that the bromine employed should be pure, as crude bromine frequently contains bromoform. If an excess of bromine has been added, it may be removed by warming the solution with a few drops of potassium hydroxide. The mixture is then distilled until no more bromoform is carried over, and the distillate, together with washings from the condenser, are mixed with 50 c.c. of alcohol and sufficient solid potassium hydroxide to make an approximately 10 per cent. solution. The mixture is heated on a water-bath in a reflux apparatus until the bromoform is completely decomposed according to the equation $3\text{CHBr}_3 + 9\text{KOH} + \text{C}_2\text{H}_5\cdot\text{OH} = 3\text{CO} + \text{C}_2\text{H}_4 + 9\text{KBr} + 7\text{H}_2\text{O}$; this operation takes about three-quarters of an hour. On cooling, the solution is exactly neutralised with dilute nitric acid, made up to 500 c.c., and titrated with *N*/10 silver nitrate, using potassium chromate as indicator. Two hundred and forty parts of bromine correspond with 58 parts of acetone. The method is suitable for the estimation of acetone in wood-spirit by using 5 c.c. of a solution of the spirit diluted to ten times its volume.

P. H.

Estimation of the Volatile Acidity of Wine. L. ROOS and W. MESTREZAT (*Ann. Chim. anal.*, 1906, 11, 41—51).—In the method proposed, the wine is evaporated under reduced pressure at a temperature of 70°—75°. When the volume of the wine has been reduced to about 2 c.c., three successive quantities of 20 c.c. of water are added and evaporated. As the acidity of the distillate is found to agree exactly with that found by subtracting the acidity of the residue from the total acidity, it is recommended that the volatile acidity be thus estimated indirectly. A number of estimations may be carried out at the same time by connecting the distillation flasks with a common receiver. Dissolved carbon dioxide should be removed from the wine before commencing the estimation. The authors find that lactic acid is not volatile under the conditions of distillation above described.

W. P. S.

General and Physical Chemistry.

Spectrum of the High Tension Arc in Air. B. WALTER (*Ann. Physik*, 1906, [iv], 19, 874—876).—The ultra-violet end of the spectrum of a high tension arc, obtained by the aid of a quartz spectrograph, exhibits a series of characteristic bands which coincide with those observed by Eder in the combustion of ammonia, and described by him as ammonia bands. They are, however, to be attributed rather to some compound of nitrogen and oxygen. J. C. P.

Phosphorescence Phenomena. ANDRÉ DEBIERNE (*Compt. rend.*, 1906, 142, 568—571).—It is suggested that when a substance P becomes phosphorescent under the influence of an exciting agent (light, cathode or X-rays, or the rays emitted by radioactive substances) it is converted into a new material, R , which is destroyed by heat, being either re-converted into P or changed into a new substance, R' . Phosphorescent light is regarded as a form of energy emitted as the result of the transformations of the substances P and R . When thermoluminescence (Becquerel, *Abstr.*, 1900, ii, 126) does not occur, R is probably an unstable substance, which is destroyed spontaneously at atmospheric temperature after its formation. The persistence of phosphorescence after the removal of the exciting agent is regarded as thermoluminescence occurring at the ordinary temperature. T. A. H.

Rotatory Power of Optically Active Substances. PAUL WALDEN (*Zeit. physikal. Chem.*, 1906, 55, 1—63).—The paper begins with a reply to Winther's criticisms (*Abstr.*, 1905, ii, 493). The author goes on to record measurements of the rotation of a large number of optically active substances, both in the pure state (at 20° and 100°) and in solution. The rotation has been determined for red, green, blue, and violet light, and this has made it possible to study the way in which the rotation dispersion coefficients and the specific and molecular rotation dispersions are related to the constitution of the various compounds. The pure substances investigated are *l*-amyl malonate, ethyl *l*-amylmalonate, *l*-amyl succinate, *l*-amyl methylsuccinate, *l*-amyl suberate, *l*-amyl glycollate, ethyl *l*-amylacetoacetate, *l*-amyl β -phenylpropionate, *l*-amyl cinnamate, *l*-amyl phenylpropiolate, *l*-amyl β -naphthoate, *l*-amyl fumarate, *l*-amyl maleate, *l*-amyl mesaconate, *l*-amyl citraconate, *l*-amyl chlorofumarate, methyl and *isobutyl* *l*-mandelates, methyl acetyl-*l*-mandelate, ethyl propionyl-*l*-mandelate, ethyl butyryl-*l*-mandelate, methyl, ethyl, *n*-propyl, *isobutyl*, and *d*-amyl *l*-malates, *l*-amyl *i*-malate, methyl, ethyl, propyl, and *isobutyl* acetyl-*l*-malates, methyl and ethyl propionyl-*l*-malates, methyl *isobutyryl*-*l*-malate, methyl, ethyl, propyl, and *isobutyl* butyryl-*l*-malates, methyl ethyl, propyl, and *isobutyl* *isovaleryl*-*l*-malates, methyl and ethyl bromoacetyl-*l*-malates, methyl and *isobutyl* *d*-chlorosuccinates, methyl *d*-bromosuccinate, methyl and ethyl chloromalates, and methyl and ethyl acetylchloromalates. Determinations of $[\alpha]_D$ for many of the foregoing substances have already been made (see Walden, *Abstr.*, 1895, i,

450 ; ii, 149 ; 1896, ii, 135, 137, 633 ; 1897, ii, 3). For the experiments with solutions, the following optically active substances were used as solutes : methyl and ethyl *l*-malates, methyl acetyl-*l*-malate, *d*-limonene, *l*-menthol, and *d*- α -monobromocamphor ; the following inactive solvents were employed : ethyl acetate, ethyl cinnamate, acetone, benzene, cinnamaldehyde, α -bromonaphthalene, chloroform, carbon disulphide, quinoline, ethyl and methyl alcohols, ether, and carbon tetrachloride.

The conclusions of a more general kind which the author draws from his study of the pure optically active substances are as follows. The rotation dispersion is a pronouncedly constitutive property, reflecting the nature and stability of the groups and elements attached to the asymmetric carbon atom. That is to say, the influence of double linking, of geometrical isomerism, of saturated and unsaturated carbon rings, of halogen atoms, &c., finds expression in the numerical values of "dispersion coefficients" and of "relative," "specific," and "molecular rotation dispersion." For a given homogeneous active substance, the dispersion coefficients a_v/a_r , a_{bl}/a_r , a_{gr}/a_r , and a_D/a_r , and the relative rotation dispersion $(a_v - a_r)/a_{gr}$ are almost independent of the temperature. The specific and molecular rotation dispersions, however, alter with temperature, increasing or decreasing according as the rotation of the substance in question increases or decreases with temperature. In homologous series of optically active substances, the individual members have practically the same dispersion coefficient and relative rotation dispersion, although the first and lowest members of a series are sometimes exceptional. The specific rotation dispersion in a homologous series is sometimes constant, sometimes shows an increase or decrease ; the molecular rotation dispersion either is approximately constant or approaches a maximum value. For a given active substance, the influence of temperature on the rotation dispersion is the same for all colours, that is, $[\alpha]_v^{100^\circ}/[\alpha]_v^{20^\circ} = [\alpha]_{bl}^{100^\circ}/[\alpha]_{bl}^{20^\circ} = [\alpha]_{gr}^{100^\circ}/[\alpha]_{gr}^{20^\circ} = [\alpha]_r^{100^\circ}/[\alpha]_r^{20^\circ}$. This temperature influence varies with the type of the active substance, and the magnitude and sign of the temperature coefficient is determined by constitutive factors. High values of the dispersion coefficient and of the relative rotation dispersion are generally found to accompany large negative temperature coefficients. High values of the dispersion coefficient and of the relative rotation dispersion are not necessarily associated with high rotatory power, although it is generally the case that a substance of very high rotatory power has also a high value of the rotation dispersion. Substances with large rotation dispersion are generally found to have a large ordinary dispersion for the same colour interval.

From the author's study of the solutions of optically active substances, the following general conclusions are drawn. For a given active solute dissolved in a given solvent, the dispersion coefficient and the relative and specific rotation dispersions are independent of the concentration of the solute. The values of the rotation dispersion of a given substance obtained in different solvents are practically equal to one another and to the value of the rotation dispersion obtained with the pure liquid substance. The observed deviations from these rules appear to be connected mainly with the special constitution and

optical properties of the solvent, these deviations being specially noticeable when the ordinary dispersion of the solvent is high. Exceptional behaviour of the optically active substance was observed most frequently in the cases in which chloroform, cinnamaldehyde, and quinoline were the solvents. It is probable that in these cases chemical reactions set in, resulting in the production of several active substances with different rotatory power and dispersion. J. C. P.

Effect of High Temperatures on Radium Emanation. WALTER MAKOWER (*Proc. Roy. Soc.*, 1906, *A*, **77**, 241—247. Compare Curie and Danne, *Abstr.*, 1904, *ii*, 306; Bronson, *Abstr.*, 1905, *ii*, 567).—The activity of radium emanation in radioactive equilibrium with its products *A*, *B*, and *C* is changed by heating above 1000°. The effect increases with the temperature up to 1200°, and possibly beyond this temperature. The effect increases with the time of heating for about the first hour, but subsequent heating is without effect. J. C. P.

Absorption of the γ -Rays of Radioactive Substances. A. S. EVE (*Phil. Mag.*, 1906, [vi], **11**, 586—595. Compare *Abstr.*, 1905, *ii*, 4).—Experiments have been made to ascertain whether the γ -rays could be taken as a measure of the total amount of radioactive matter present in a given substance. The substances examined were placed on a platform about 7 cm. below the electroscope employed and layers of lead were introduced between this and the active substance. The γ -rays from radium, uraninite, thorium, and radio-thorium are absorbed at the same rate by lead. On the other hand, uranium emits γ -rays which are much more readily absorbed; they are fewer in number and appear to be homogeneous. The more penetrating rays of actinium appear to be of two kinds ($\lambda = 4.1$ between 0.45 and 2.8 mm. of lead and $\lambda = 2.7$ to 2.0 from 2.8 to 8.7 mm. of lead).

It is suggested that a kilogram of thorium nitrate sealed in a thin glass vessel of 16 cm. diameter and placed under a layer of lead 1 cm. thick might be adopted as a convenient standard for measuring the quantity of radium or thorium in a given mass of ore. It has been ascertained that about 18 per cent. of the γ -rays from this quantity of thorium nitrate are lost by self-absorption. H. M. D.

Specific Action of Metals in Electric Discharge by X-Rays and Secondary Rays. Rôle of the Metal in the Transformation of X-Rays into Secondary Rays. DRAGOMIR HURMUZESCU (*Ann. sci. Univ. Jassy*, 1906, **3**, 258—287).—A metallic plate connected with the electrometer was exposed to the action of X-rays and the rate of discharge investigated, plates of different metals being used. The apparatus employed and experimental details are described. The order of activity of the metals examined was as follows: lead, iron, silver, tin, aluminium. The effect of different metals in producing secondary rays was next investigated. The X-rays were allowed to fall upon metallic plates, and the electrometer plate, shielded from the direct X-rays, was exposed to the action of the secondary rays. It was found that the metals employed were separable into groups, although differences occur between the activity of the metals in each group. The most active group comprised the metals nickel, cobalt, copper, iron, and zinc; the

next group contained lead, cadmium, bismuth, and silver; the third, aluminium and magnesium. Tin occupies a place between the second and third groups, but is nearer to the second. The results are briefly discussed by the author.

L. M. J.

Experiment to show the Fluorescent Action of the Secondary Rays caused by Radium. K. SIEGL (*Chem. Centr.*, 1906, i, 902; from *Physikal. Zeit.*, 7, 106—107).—A radium preparation enclosed in a lead capsule in which there is a mica window is placed on a platinum-barium cyanide screen. When reflecting plates are brought within 1—2 cm. of the capsule, the screen becomes illuminated. Wood has the least secondary radiation, and then follow in order of increasing activity, aluminium, ebonite, glass, iron, nickel, copper, zinc, silver, tin, platinum, gold, mercury, and lead. Since the radiation does not increase with the sp. gr., but varies more nearly in proportion to the atomic weight, thorium and uranium should possess the greatest reflecting power. Since the intensity of the fluorescence increases with the thickness of the plate, the effect is not merely due to superficial reflection. When plates of absorbing substances such as ebonite are placed between the capsule and the reflector, the decrease of intensity is greater in the case of aluminium than of lead; in the former case, the secondary rays are caused by β -rays which differ from those in the latter in being more readily absorbed. The secondary rays of all substances appear, however, to possess the same penetrating power.

E. W. W.

β -Polonium. FRIEDRICH GIESEL (*Ber.*, 1906, 39, 1014. Compare this vol., ii, 212).—The author's β -polonium is identical with Rutherford's radium E, the activity of which decreases to half value in six days (*Abstr.*, 1905, ii, 664).

G. Y.

Electrical Conductivity of Metallic Oxides. F. HORTON (*Phil. Mag.*, 1906, [vi], 11, 505—531).—The variation of the electrical conductivity of several metallic oxides with temperature has been investigated with a view to ascertaining whether the conduction is electrolytic or metallic in character. The oxides were employed in the form of slabs about one sq. cm. in area and 1—2 mm. thick, these being placed between stout platinum plates firmly pressed together and heated in an electric furnace. The oxides of calcium, barium, and magnesium, bismuth trioxide, lead monoxide, cupric oxide, sodium peroxide, and quartz were experimented on. The conductivity of calcium oxide increases rapidly with rise of temperature, and the curves representing the connection between them are exactly similar to those obtained by Wehnelt for the relation between the number of corpuscles emitted by calcium oxide and the temperature.

The conductivity of magnesium oxide increases rapidly with the temperature up to 1200—1250° and then decreases. If the temperature is kept constant above 1200°, the conductivity also decreases with the time. The phenomenon is probably due to a change of the oxide into a less conducting form of greater density. The temperature conductivity curves of the other oxides are similar to those of calcium.

Polarisation, indicative of electrolytic conduction, was observable on

the passage of a current through calcium oxide at temperatures above 800° . A smaller polarisation effect was also obtained with the other oxides excepting cupric oxide. Measurements of the amount of electrolytic conduction were made by coating the negative electrode in a discharge tube with calcium, barium, or cupric oxide, and determining the alteration in pressure in the tube after the passage of a known quantity of electricity. The results obtained indicate that in the case of calcium and barium oxides only an extremely small fraction of the total current is carried by electrolytic ions, and in the case of cupric oxide such conduction appears to be entirely absent. In opposition to Nernst's views, the author concludes that the conductivity of the oxides is metallic: that is, the current is carried by negatively-charged corpuscles.

H. M. D.

Formation of Hydrogen Peroxide and other Compounds by means of the Tesla Discharge. ALEXANDER FINDLAY (*Zeit. Elektrochem.*, 1906, 12, 129).—A mixture of steam and air exposed to the Tesla discharge usually yields a quantity of hydrogen peroxide which can be recognised by the titanium dioxide reaction. Evidence of the formation of nitric acid from a mixture of oxygen and nitrogen, of sulphur trioxide from a mixture of sulphur dioxide and oxygen, of ammonia from a mixture of hydrogen and nitrogen, and of hydrazine from a mixture of ammonia and nitrogen in the same circumstances was also obtained.

T. E.

Anodic Solution of Hydrogen and its Passivity. OTTO SACKUR (*Zeit. physikal. Chem.*, 1906, 54, 641—664).—The residual current cannot be calculated so easily in the case of the cell $\text{Pt}_H | \text{H}_2\text{SO}_4 | \text{Pt}_H$ (Pt_H = platinum charged with hydrogen) as is possible in other cases (see Nernst and Merriam, *Abstr.*, 1905, ii, 674). The velocity of the anodic solution of hydrogen, that is, the process resulting in the conversion of the molecule H_2 into the ion H^+ , is not high compared with the velocity of diffusion (see *loc. cit.*). The velocity of this anodic solution of hydrogen for a given applied *E.M.F.* falls off with time, and the greater the *E.M.F.* applied the more rapid is the decrease. The initial velocity of the anodic solution of hydrogen increases with the applied *E.M.F.* up to 0.7 volt, falling thereafter to very low values. That is to say, polarisation to the level of the oxygen potential checks the oxidation of hydrogen. This behaviour of hydrogen is very similar to the phenomenon of passivity exhibited by metals.

All the observed phenomena are adequately interpreted by the view that the anodic oxidation of hydrogen depends on combination with the discharged oxygen, promoted by the catalytic activity of the platinum electrode, and that this catalytic activity is markedly impaired when anodic charging with oxygen takes place. In harmony with this view, it is shown that the combination of hydrogen and oxygen is accelerated by platinum charged with hydrogen; platinum charged with oxygen, on the other hand, has but a slight catalytic influence.

The cathodic reduction of oxygen is accelerated by charging the electrode with hydrogen.

J. C. P.

Theoretical Considerations on Electrolytic Dissociation. Influence of the Solvent on the Stability of the Dissolved Molecules. M. BRILLOUIN (*Ann. Chim. Phys.*, 1906, [viii], 7, 289—320).—A theoretical paper. M. A. W.

Potential of the Oxygen Electrode. GILBERT N. LEWIS (*J. Amer. Chem. Soc.*, 1906, 28, 158—171).—A résumé is given of previous work on the determination of the potential of the oxygen electrode and it is shown that the values obtained hitherto are probably too low.

A new form of silver electrode has been prepared by heating a platinum spiral in a tube with silver oxide in such a manner that the spiral becomes entirely coated with a loosely coherent mass of finely-divided silver. This electrode has been compared with that recommended by Goodwin, which consists of silver foil electro-plated with silver, and it is found that the two kinds of silver have different potentials, the plated electrode being the more negative.

The *E.M.F.* of a cell of the type $\text{Ag}, N/10 \text{ AgNO}_3, N/10 \text{ KNO}_3, N/10 \text{ KCl}, \text{HgCl}$, was measured and found to be -0.391 volt at 30° . The temperature coefficient of this *E.M.F.* between 30° and 0° was found to be 0.00121 volt per degree.

From the potential of the silver electrode, the decomposition pressure of silver oxide (this vol., ii, 284), and the solubility of silver oxide, the true potential at 25° of an oxygen electrode against the normal hydroxyl ion is found to be -0.674 volt (the normal electrode at 18° being taken as -0.560 volt). From this value and the electrolytic dissociation of water, the true *E.M.F.* at 25° of the oxygen-hydrogen cell has been calculated and found to be 1.217 volts, a value which agrees closely with that recently calculated by Nernst (this vol., ii, 17) from the dissociation of water-vapour. The temperature coefficient of the oxygen electrode has also been calculated.

E. G.

The Factor of Proportionality between the Mobility and Absolute Velocity of Ions. LUDWIK BRUNER (*Zeit. Elektrochem.*, 1906, 12, 188).—Calling l the mobility of an ion and u its velocity, we have $l = \text{const.} \times u$. Since $l = \text{conductivity/concentration}$, its dimensions are $\text{cm.}^3/\text{ohm cm. equiv.}$, also $u = \text{velocity/fall of potential per unit length}$, and its dimensions are cm./sec. volt . Hence, the dimensions of the constant are coulombs/equivalents, that is 96540.

T. E.

Genesis of Ions by Collision and Sparking-potentials in Carbon Dioxide and Nitrogen. H. E. HURST (*Phil. Mag.*, 1906, [vi], 11, 535—552).—The currents between two parallel zinc plates immersed in an atmosphere of carbon dioxide or nitrogen have been measured when the negative plate was subjected to the influence of ultra-violet light and when the electric intensity between the plates, their distance apart, and the pressure of the gas were varied. The observed values as well as those of the sparking-potentials are in agreement with the theoretical formula previously given.

A comparison of the results with the two gases in the light of this

theory shows that the number of new ions produced by a negative ion in travelling through one centimetre of the gas is approximately the same for both gases, but the number of new ions produced by a positive ion is much smaller in carbon dioxide than in nitrogen. It is calculated that under the same conditions a negative ion makes about 2400 times as many new ions in carbon dioxide as a positive ion, whereas in nitrogen the ratio is only 22. From this it is inferred that the positive ions differ more from the negative ions in the case of carbon dioxide than in that of nitrogen, and, since all negative ions are the same, it would seem that the positive ions in carbon dioxide are much larger than those in nitrogen.

H. M. D.

Ions of Pure Water. JAMES WALKER (*Trans. Faraday Soc.*, 1906, 1, 362—364).—In deducing the temperature coefficient of the conductivity of water, the variation of the ionic concentration as well as that of the mobility of the hydrogen and hydroxyl ions with the temperature must be taken into consideration. The variation of the ionic concentration of pure water can be calculated by means of van't Hoff's thermodynamic formula from the heat of neutralisation of a strong acid by a strong base. The calculated temperature coefficient of the conductivity is then given by $K = K_{18} (1 + 0.060 T + 0.0014 T^2)$, which is in perfect agreement with the equation found experimentally by Kohlrausch for the purest water he could prepare. This agreement justifies the assumption that the hydrogen and hydroxyl ions and no others are responsible for the conductivity of pure water.

H. M. D.

Cathode Potential and Electrolytic Reduction in Sulphuric Acid Solutions. JULIUS TAFEL (*Zeit. Elektrochem.*, 1906, 12, 112—122. Compare Abstr., 1901, ii, 588; 1905, ii, 223, 224, and 569; this vol., ii, 216).—An account of the main results obtained in the papers referred to.

T. E.

Electrolytic Reduction of Molybdic Acid in Acid Solutions. ALBERTO CHILESOTTI (*Zeit. Elektrochem.*, 1906, 12, 146—166 and 173—183).—The solution of molybdic acid is placed in a porous cell on the bottom of which the cathode lies. Part of the current reduces the molybdic acid, part of it produces hydrogen; by comparing the quantity of hydrogen evolved with that produced in a voltameter in the same circuit, the current efficiency at any period of the electrolysis is obtained. The electrolysis is always carried on until the current efficiency sinks to zero, and curves are given showing the current efficiency during the whole progress of the experiment. The effect of current density is first studied with a solution containing about 3.5 per cent. of molybdenum trioxide dissolved in 9*N*-hydrochloric acid and a mercury cathode. It is found that at higher current densities a larger fraction of the current is employed in liberating hydrogen; although the time required for complete reduction is shorter. Increasing the concentration of the molybdic acid increases the current efficiency to some extent. The concentration of the hydrochloric acid has a curious effect on the curve of current efficiency; with 9*N*-acid,

the current efficiency is at first 100, falling subsequently regularly to zero. With 4*N*-acid, the curve again begins at 100, but soon falls very rapidly to about 10 and then rises slowly to a maximum at 29, thereafter falling to zero. With weaker acid, the curve follows a similar course, but the maximum occurs sooner and at a much higher value of the current efficiency. The probable explanation of this is that a film of oxide is first formed on the cathode, which acts as a diaphragm and prevents reduction; later this film is dissolved or reduced to metal and metallic molybdenum amalgam is formed on the surface of the cathode, the reducing action of the amalgam being much greater than that of the mercury alone. It is known that molybdenum amalgam is formed in presence of dilute acid, but not in concentrated acid. Rise of temperature increases the current efficiency considerably. The material of the cathode has a great effect on the current efficiency. Using a solution of 3.5 per cent. of molybdenum trioxide in 4*N*-hydrochloric acid, a current density of 0.042 ampere per sq. cm. at 10—20°, the average current efficiencies were, with platinised platinum, 10.6 per cent., mercury, 18.9 per cent., smooth platinum, 51.7 per cent., tin, 66.9 per cent., lead, 74.5 per cent. In 9*N*-hydrochloric acid, tin gave the best result, lead and platinum slightly worse results, and mercury was worst of all. The behaviour of these metals has obviously no connection with the super-tension required to liberate hydrogen on their surfaces; it would rather appear to be connected with their solubility, both lead and tin being found in solution after the electrolysis, which was not the case with platinum and mercury. The molybdic acid is always reduced to tervalent molybdenum compounds except when a platinised platinum cathode is used; in this case, the reduction stops at the quinquevalent stage. Solutions in sulphuric and oxalic acids are also investigated with similar results, the tin cathode being insoluble in the oxalic acid solution, and the lead cathode insoluble in the sulphuric acid solution gave results similar to those obtained with platinum.

In the second part of the paper, the potential difference between platinum and the solution at different stages of the reduction is examined. In all cases investigated the same general result was obtained. The potential difference increases slowly as the reduction proceeds, until the whole of the molybdenum is in the quinquevalent condition; it then rises very suddenly to a higher value, after which it again increases slowly until the molybdenum is almost reduced to the tervalent state, when a further rather sudden increase occurs. During the first stage of the reduction, the potential is doubtless conditioned by the process $\text{MoO}_4'' + 8\text{H}^+ \rightleftharpoons \text{F} = \text{Mo}^{\cdots\cdots} + 4\text{H}_2\text{O}$; during the second stage, the main change is probably the reduction of quinquevalent to tervalent molybdenum. The final increase is possibly due to the formation of bivalent molybdenum ions.

With regard to the colour of the solutions, the solutions in 7*N*- to 9*N*-hydrochloric acid first become emerald-green owing to the formation of complex compounds of the oxychloride, MoOCl_3 ; they then become brown and finally orange-red, and contain complex compounds of the formula $(\text{MoCl}_3)_n\text{HCl}$. The solutions in more dilute hydrochloric acid change, when the reduction is almost complete, from a

brownish-red colour to a deep olive-green colour. The green solutions are unstable; they decompose water, taking up oxygen and becoming brownish-red again. Both the red and the green solutions contain molybdenum trichloride, and the author supposes that they are related in the same way as the green and violet solutions of chromic chloride. The solutions in sulphuric acid behave similarly. The change from one modification to the other is possibly due to the presence of traces of molybdenum dichloride.

T. E.

Relation of Stability to Electrochemical Efficiency in Hypochlorite Production. W. POLLARD DIGBY (*Trans. Faraday Soc.*, 1906, 1, 326—332).—The factors which contribute to the rapid falling off in the yield of available chlorine per kilowatt hour as the amount of available chlorine in the solution increases have been examined. By taking 50 per cent. as the critical point in the fall of the current efficiency, the concentration of available chlorine which can be attained before this point is reached increases with increasing density of the sodium chloride solution. The rapid loss of available chlorine exhibited by certain electrolytic bleaching liquors and the low efficiency of the process of production have been in part traced to metallic impurities. One part of iron per 100,000 parts of water has a marked effect on the depreciation of the liquor.

H. M. D.

Amphoteric Electrolytes. HARALD LUNDÉN (*Zeit. physikal. Chem.*, 1906, 54, 532—568. Compare Winkelblech, *Abstr.*, 1901, ii, 370; Hantzsch and Barth, *Abstr.*, 1902, i, 222; Hantzsch, *Abstr.*, 1904, i, 381; Walker, *Abstr.*, 1904, ii, 309; 1905, ii, 138).—The author has determined at various temperatures the dissociation constants (both acidic and basic) of *i*- β -asparagine, *o*-aminobenzoic acid, and acetoxime. The methods adopted were the catalysis and saponification of ethyl acetate, the acidic dissociation constant of *o*-aminobenzoic acid being determined from the conductivity. The values of the dissociation constants increase rapidly as the temperature rises, a feature which characterises all ordinary weak electrolytes hitherto studied. It is therefore incorrect to speak, as Hantzsch does, of an abnormally large temperature-coefficient in the case of pseudo-acids.

According to the author, Walker's theory of amphoteric electrolytes cannot explain the simultaneous occurrence of slight hydrolysis and slight conductivity, since the diminution of conductivity resulting from the removal of hydrogen or hydroxyl ions by a basic or acid group is compensated by the formation of complex anions and cations.

The simultaneous occurrence of slight hydrolysis and slight conductivity may be due to the substance being either an amphoteric electrolyte or capable of forming with sodium hydroxide or hydrochloric acid salts which are derived from a differently constituted compound. This last explanation applies in the case of the nitro-paraffins, the first in the case of the ketone oximes.

The author has determined the solubility of *o*-aminobenzoic acid in solutions of barium nitrate and chloride, potassium nitrate, iodide, and

chloride. It appears probable from these determinations that a simultaneous neutralisation of the two groups of the amphoteric electrolyte takes place. The curves obtained by plotting the relative increase of solubility of the *o*-aminobenzoic acid against the concentration of the salt exhibit maxima. There is a parallelism between these changes of solubility and the effects of normal salts on the catalysis and saponification of ethyl acetate.

J. C. P.

New Electrical Arrangement of the Breslau University Chemical Laboratory. RICHARD ABEGG (*Zeit. Elektrochem.*, 1906, 12, 109—112).—A description of the switch board for distributing current from a battery of accumulators to the working places in the laboratory and to the lecture room.

T. E.

Heusler's Magnetic Alloy of Manganese, Aluminium, and Copper. ANDREW GRAY (*Proc. Roy. Soc.*, 1906, A, 77, 256—259. Compare Fleming and Hadfield, *Abstr.*, 1905, ii, 799).—A rod containing about 16 per cent. of manganese, 8 per cent. of aluminium, a little lead, and the rest copper, was found to be almost non-magnetic. After heating at 340° for about twenty minutes, its magnetic properties were much more pronounced. The critical temperature being about 350°, heating at 400° and immersion in cold water practically destroyed the magnetic quality. When the quenched alloy, however, was tested at the temperature of liquid air, it was found to be more susceptible to magnetism than in its previous best condition, whilst exhibiting much less hysteresis and retentiveness.

J. C. P.

Equilibrium of Binary Solutions of Phenols and Amines. ROBERT KREMANN (*Monatsh.*, 1906, 27, 91—107. Compare Schreinemakers, *Abstr.*, 1899, ii, 739; 1900, ii, 135).—The melting-point curves of mixtures of aniline with *o*-, *m*-, and *p*-cresol and of phenol with *o*- and *p*-toluidine, *m*-xylidine, and β -naphthylamine show that in each case there is formed a 1 : 1 molecular additive compound, which is represented on the curve by a maximum lying between two eutectic points. The curve for mixtures of aniline and *o*-cresol has eutectic points at 0° and -20° for mixtures containing 31 and 83 mol. per cent. respectively of aniline; the maximum between the eutectic points is 8.3°. The curve for mixtures of aniline and *p*-cresol has eutectic points at 6° and -16° for mixtures containing 27 and 89 mol. per cent. respectively of aniline; the maximum is 19.2°. The curve for mixtures of aniline and *m*-cresol has two eutectic points at -30° for mixtures containing 30 and 77 mol. per cent. respectively of aniline; the maximum is -14.6°.

Mixtures of phenol and *p*-toluidine give a curve with eutectic points at 17° and 10° for mixtures containing 32 and 75 mol. per cent. of *p*-toluidine; the maximum is 29°. The curve for mixtures of phenol and *o*-toluidine has a eutectic point at 10° for a mixture containing 19 mol. per cent. of *o*-toluidine; the second eutectic point was not observed; the maximum is 34°. The curve for mixtures of phenol and *m*-xylidine has eutectic points at -2° and -25° for mixtures

containing 28 and 80 mol. per cent. of the xylidine; the second eutectic point was found by extrapolation; the maximum is 16° . The curve for mixtures of phenol and β -naphthylamine has eutectic points at 35° and 82.5° for mixtures containing 4 and 58 mol. per cent. of β -naphthylamine; the maximum is 83.5° .

Mixtures of phenol and dimethylaniline give curves falling from the melting points of dimethylaniline and of phenol to -32.5° and -5.5° for mixtures containing 49 and 67.4 mol. per cent. respectively of phenol; intermediate mixtures containing 50—67 mol. per cent. of phenol could not be solidified. G. Y.

The Limit of Stability of Additive Compounds in the Solid State and the Divergence of the Same from Kopp and Neumann's Law. ROBERT KREMANN and R. VON HOFMANN (*Monatsh.*, 1906, 27, 109—124. Compare Kremann, Abstr., 1905, ii, 76).—The specific heats of additive compounds when determined by cooling from temperatures only a few degrees below the solidifying points are found to be greater than those calculated according to Kopp and Neumann's law. The divergence, which is the greater the nearer the initial temperature is to the solidifying point, is caused by the additive compound being in a state of partial fusion below its solidifying point; in the fused substance, the additive compound is in equilibrium with its components. The excess of the observed specific heat over the calculated is composed of, but is not the sum of, the heat of fusion of one or both components, the heat of dissociation of the additive compound, and the heat of solution of the compound in one or both of its components. On the other hand, results agreeing closely with the calculated are obtained if the initial temperature is far enough below the solidifying point.

The amount of heat expressed in gram-calories, lost by seven additive compounds in cooling from various initial temperatures to 0° , and that calculated by Kopp and Neumann's law, are given in a series of tables, the following extracts from which indicate the main results:

Phenol-*p*-toluidine, m. p. 29° : 1 gram cooled from 29.6° , 28.25° , 23.95° , and 16.5° gave 21.78, 10.79, 3.15, and 0.43 gram-calories respectively in excess of the calculated.

Phenol-aniline, m. p. 31° : 1 gram cooled from 29.5° , 28.3° , and 16.55° gave 16.11, 8.14, and 1.47 gram-calories respectively in excess of the calculated.

Phenol-picric acid, m. p. 85° : 1 gram cooled from 83.75° , 79.4° , and 19.1° gave 14.8, 5.51, and 0.16 gram-calories respectively in excess of the calculated.

Dinitrophenol-naphthalene, m. p. 91.7° : 1 gram cooled from 90.1° and 64.2° gave 3.09 and 0.52 gram-calories respectively in excess of the calculated.

Trinitrotoluene-naphthalene, m. p. 96.5° : 1 gram cooled from 94.1° and 55.6° gave 1.44 and 0.13 gram-calories respectively in excess over the calculated.

2:5-Dinitrotoluene-naphthalene, m. p. 60° : 1 gram cooled from 58.3° gave 1.31 gram-calories in excess of, but when cooled from 45.2° gave 0.04 gram-calorie less than, the calculated.

Calcium chloride hexahydrate, m. p. 30.2° : 1 gram cooled from 28.4° and 16.5° gave 4.96 and 0.69 gram-calories respectively in excess of the calculated.

The results are expressed also in curves, which show that Kopp and Neumann's law holds good at $10-0^{\circ}$, at which temperatures these additive compounds are practically not dissociated. G. Y.

Influence of Substitution in the Components on the Equilibrium of Binary Solutions. II. ROBERT KREMANN and O. RODINIS (*Monatsh.*, 1906, 27, 125—179. Compare Abstr., 1905, ii, 77).—The melting-point curve for mixtures of aniline and *o*-nitrophenol falls to a eutectic point at -13.5° for a mixture containing 14.2 mol. per cent. of *o*-nitrophenol. The curve for mixtures of *p*-nitrophenol and aniline falls from the melting point of *p*-nitrophenol to a break at 42° , representing an additive compound of equal molecules, and then to a eutectic point at -21° for a mixture containing 11 mol. per cent. of *p*-nitrophenol. The curve for mixtures of aniline and *m*-nitrophenol falls from the melting point of *m*-nitrophenol to 22.5° , where there is a break representing the 1:1 molecular additive compound, and then to a eutectic point at -15° for a mixture containing 19 mol. per cent. of *m*-nitrophenol.

Mixtures of carbamide and phenol give a curve which falls from the melting point of carbamide to a break at 61° , representing Eckenroth's compound of 2 mols. of phenol with 1 mol. of carbamide (Abstr., 1886, 946), and again to a eutectic point at 37° for a mixture containing 94.8 mol. per cent. of phenol. The curve for mixtures of carbamide and *p*-nitrophenol has eutectic points at 89.5° and 108.5° for mixtures containing 22.8 and 68.1 mol. per cent. respectively of carbamide; the maximum between the eutectic points is 116° , and represents the 1:1 molecular additive compound. The curve for mixtures of carbamide and *m*-nitrophenol falls from the melting point of carbamide to a break at 80.5° representing the 1:1 molecular additive compound, and then to a eutectic point at 69° for a mixture containing 29 mol. per cent. of carbamide. The curve for mixtures of carbamide and *o*-nitrophenol shows that only 1.5 mols. of *o*-nitrophenol are soluble in 98.5 mols. of carbamide, whilst only 3 mols. of carbamide are soluble in 97 mols. of *o*-nitrophenol, all other mixtures consisting of two liquid phases: a saturated solution of carbamide in *o*-nitrophenol and a saturated solution of *o*-nitrophenol in carbamide. Carbamide separates from the first of these phases at 125° , whilst the second diminishes with each addition of carbamide.

The curve for mixtures of naphthalene and *o*-dinitrobenzene has a eutectic point at 62.5° for a mixture containing 67.5 mol. per cent. of naphthalene. The curve for mixtures of naphthalene and *p*-dinitrobenzene falls from the melting point of the dinitrobenzene to a break at 118° , representing the 1:1 molecular additive compound.

Mixtures of phenol with *m*-, *o*-, and *p*-nitroanilines give melting-point curves which have eutectic points at 28.8° , 11° , and 34° for mixtures containing 15.7, 35.9, and 8.3 mol. per cent. of the nitroaniline respectively.

The curves for mixtures of picric acid and *o*-, *m*-, and *p*-nitrophenols

have eutectic points at 34.5° , 72.8° , and 79° for mixtures containing 77.1, 58.8, and 52.3 mol. per cent. of the nitrophenol respectively.

The curve for mixtures of aniline and *o*-dinitrobenzene has a eutectic point at -8.5° for a mixture containing 3.5 mol. per cent. of the dinitrobenzene. The curve for mixtures of aniline and *p*-dinitrobenzene has no break between 143.5° and 15° , representing mixtures containing 61 to 9 mol. per cent. of the dinitrobenzene.

The curves for mixtures of naphthalene and *p*- and *m*-chloronitrobenzenes have eutectic points at 43.8° and 23° for mixtures containing 51.6 and 64.5 mol. per cent. of the *p*- and *m*-compounds respectively.

Mixtures of aniline and *p*- and *m*-chloronitrobenzenes give curves having eutectic points at -18° and -12° for mixtures containing 82 and 87.6 mol. per cent. respectively of aniline.

The curve for mixtures of aniline and quinol has a break at about 90° representing the 2 : 1 additive compound. The curve for mixtures of aniline and catechol falls from the melting point of catechol to a break at 39° representing the 1 : 1 molecular additive compound, and to a eutectic point at -15° for a mixture containing 88.7 mol. per cent. of aniline. Mixtures of aniline and resorcinol containing less than 54.5 mol. per cent. of resorcinol do not solidify.

Mixtures of naphthalene with 2 : 6- and 3 : 4-dinitrotoluene give curves which have eutectic points at 35° and 31° for mixtures containing 58.1 and 59.6 mol. per cent. of the 2 : 6- and 3 : 4-dinitrotoluenes respectively. The curve for the mixture of naphthalene and 3 : 5-dinitrotoluene has eutectic points at 56° and 58.8° for mixtures containing 31.1 and 66.9 mol. per cent. respectively of the dinitrotoluene; the maximum 63.2° between the eutectic points represents the 1 : 1 molecular additive compound.

The curves for mixtures of aniline and 2 : 6- and 3 : 4-dinitrotoluene have eutectic points at -13° and -14° for mixtures containing 11.2 and 19.2 mol. per cent. of the dinitrotoluenes respectively. The curve for the mixture of aniline and 3 : 5-dinitrotoluene falls from the melting point of the dinitrotoluene to a break at 44.5° , representing the 1 : 1 molecular additive compound, and then to a eutectic point at -9.2° for a mixture containing 19.2 mol. per cent. of the dinitrotoluene.

G. Y.

Latent Heats of Vaporisation of Liquid Oxygen and Liquid Nitrogen, and the Variation of these Quantities with Temperature. HEINRICH ALT (*Ann. Physik*, 1906, [iv], 19, 739—782).—The earlier investigation (Abstr., 1904, ii, 393) has been extended, and with improved apparatus, of which full details are given, the author has obtained somewhat different values for the latent heats of vaporisation (*r*) of liquid oxygen and liquid nitrogen. Thus for oxygen at -182.93° (the boiling point under normal pressure), $r = 50.92$ cal.; at -194° , $r = 53.23$ cal.; at -205° , $r = 55.52$ cal. For nitrogen at -195.55° (the boiling point under normal pressure), $r = 47.65$ cal.; at -202° , $r = 49.42$ cal.; at -210° , $r = 51.61$ cal.

J. C. P.

Calorimetry of Volatile Liquids. WALTER ROSENHAIN (*J. Soc. Chem. Ind.*, 1906, 25, 239—241).—The calorific value of volatile

liquids has been determined by burning pellets of compressed cellulose saturated with these liquids in the coal calorimeter designed by the author (*Phil. Mag.*, 1902, [vi], 4, 451). In order to reduce the loss of liquid from evaporation during weighing, the pellets were wrapped in a coating of thin tinfoil. The calorific values of the pellet and of the tinfoil wrapping were allowed for in calculating the results of an experiment.

P. H.

Thermochemistry of Phenylsazones and Phenylhydrazones of the α -Diketones and Reducing Sugars. PHILIPPE LANDRIEU (*Compt. rend.*, 1906, 142, 580—582. Compare Abstr., 1905, ii, 628).—The heats of combustion of these substances were determined in the calorimetric bomb, and from the results the heats of formation and the amounts of heat developed in the addition of the first and second mols. of phenylhydrazine were calculated. The results, expressed in Calories, are as follows; the figures are in each case given in the following order: (1) heat of combustion, (2) heat of formation, (3) heat developed in the addition of the first mol. of phenylhydrazine in the case of phenylhydrazones, or of the second mol. in the case of phenylsazones.

Diacetylphenylhydrazone, 1356.9, 0.1, and 19.6. Diacetylphenylsazone, 2219, -90.1, and 8.8. Benzilphenylhydrazone, 2491.6, -53.6, and 13.6. Benzilphenylsazone, 3356, -146, and 7.6. Benzoinphenylhydrazone, 2530.1, -23.1, and 15.2. Glyoxalphenylsazone, 189.3, -90, and 25 (in this case, 25 Cal. is the heat developed in the addition of 2 mols. of phenylhydrazine).

The phenylhydrazones of the following sugars gave the under-mentioned results: arabinose, 1421, 168, 8.6; dextrose, 1540, 212.6, 10; galactose, 1536, 216.6, and 6.7; lævulose, 1544 (?), 208.6, and 4.7; mannose, 1538, 214.6, and 12; maltose, 2215, 448.4, and 10.3, and lactose, 2211.5, 451.9, and 14.5.

The osazones of the sugars gave the following results. In these cases the third figure is the heat developed in the reaction: sugar + phenylhydrazine (2 mols.) = phenylsazone + $2\text{H}_2\text{O}$ + H_2 . Arabinose, 2220, 73.1, and 13.7. Xylose, 2228, 65.1, and 93. Dextrose, lævulose, mannose, 2353, 103.4, and 1.2, 0.5, and 1.2 respectively. Galactose, 2354, 102.4, and -7.5. Maltose, 3036, 331.2, and -6.9. Lactose, 3039, 328.2, and -9.2.

The heats of combustion and formation of diacetyl are 503.7 and 80.5 Cal., and the corresponding constants for benzil are 1632.1 and 33.1 respectively.

Lævulosephenylhydrazone, prepared by the action of phenylhydrazine on the sugar dissolved in alcohol, is a white, readily-crystallisable powder. *Maltose phenylhydrazone*, similarly prepared, is a white hygroscopic powder, which melts and decomposes at 130° .

T. A. H.

Equation of an Ideal Eutectic Curve in a Ternary System, and the Use of this Equation in Calculating the Transition Temperature of Two Isomerides in Presence of Solution. JOHANNES J. VAN LAAR (*Zeit. physikal. Chem.*, 1906, 55, 64—70).—A theoretical paper.

J. C. P.

Determinations of Vapour Density by Nernst's Modification of Victor Meyer's Method. LEO LÖWENSTEIN (*Zeit. physikal. Chem.*, 1906, 54, 707—714).—The apparatus used was similar to that described by Nernst (Abstr., 1903, ii, 636), except that it was constructed of platinum instead of iridium. The method of introducing the weighed substance has also been modified. With this apparatus satisfactory results were obtained for the molecular weights of carbon dioxide and mercury at 1350°.

The dissociation of carbon dioxide at high temperatures was studied by filling the apparatus with the gas and then dropping in a small piece of an easily oxidisable metal such as aluminium. In this way, enough carbon monoxide was produced to repress the dissociation of the carbon dioxide with practical completeness, and from the observed diminution in volume the dissociation of the latter gas could be calculated. The author finds that carbon dioxide is dissociated at 1550° to the extent of 0.4 per cent. J. C. P.

The Gaseous-liquid State. II. A. N. SCHÜKAREFF (*Zeit. physikal. Chem.*, 1906, 55, 99—112. Compare Abstr., 1903, ii, 710).—An apparatus is described whereby the heat of condensation of superheated vapours can be determined. The vapour of the substance in question is led through a bulbed tube packed with metal turnings and surrounded with the vapour of a liquid of high boiling point, and passes thence into the condenser of the calorimeter. In this way, the author has determined Q' (heat of condensation of 1 gram-molecule at the ordinary pressure after allowance has been made for the work done on the vapour during condensation) for ether, *iso*amylene, and *isopentane* over several temperature intervals. He has also determined the heat given out by the substance during the same temperature interval when it is enclosed in a small sealed capsule. If this heat (referred to 1 gram-molecule) is indicated by Q , then $Q' - Q$ represents the heat absorbed when the substance expands from a very small to a very large volume. The variation of $Q' - Q$ with the mean density (D) of the contents of the capsule is deduced for the three substances mentioned. When Q is plotted against D , isothermals are obtained which, below a certain temperature, are convex to the horizontal axis, above it are concave. At this temperature, therefore, which lies considerably above the critical temperature, the variation of internal energy with the volume can be represented by a straight line, in harmony with van der Waals' equation. It is suggested that this special temperature should be called the van der Waals temperature; for ether it is slightly below 240°, for *isopentane* it is about 300°. J. C. P.

The Gaseous-liquid State. III. A. N. SCHÜKAREFF and MARIE TSCHUPROWA (*Zeit. physikal. Chem.*, 1906, 55, 125—127. Compare Abstr., 1903, ii, 710, and preceding abstract).—A mixture of *isopentane* and ether in molecular proportions has been studied at 235° on the lines already described. It appears that the internal energy of the mixture is approximately equal to the sum of the internal energies of the components when the volume of the mixture is equal to the sum of the volumes of the components. The value of a/A (a = the constant in van

der Waals' equation, A = mechanical equivalent of heat) is nearly independent of the mean density in the case of pure ether and also in the case of the mixture.

J. C. P.

Critical Temperatures of Solutions. II. MIECZYSLAW CENTNERSZWER and M. ZOPPI (*Zeit. physikal. Chem.*, 1906, **54**, 689—706. Compare Abstr., 1904, ii, 158).—The authors have determined the critical temperatures for mixtures of ether and methyl alcohol, and find that Straus and Pawlewski's rule is not even approximately fulfilled. The observed critical temperatures are in all cases lower than the values calculated by the mixture rule, and some of them are actually lower than the critical temperature of pure ether. The critical curve, therefore, exhibits a minimum, and it is noteworthy that the boiling-point curve for mixtures of ether and methyl alcohol, also exhibits a minimum. All mixtures of ether and methyl alcohol, the concentrations of which lie between that of the minimum critical temperature and methyl alcohol, exhibit retrograde condensation of the first order. The critical point is shown to be a point of inflexion on the density—temperature curve. The law of the rectilinear diameter appears to be applicable in the case of mixtures of ether and methyl alcohol. The densities of mixtures of these two liquids have been determined at 25°, and it is shown that mixture is accompanied by considerable contraction. The paper contains a list of the critical curves of mixtures recorded up to the present time.

J. C. P.

Determination of the Coefficient of Internal Friction of Gases by a New Experimental Method. GYÖZÖ ZEMPLÉN (*Ann. Physik*, 1906, [iv], **19**, 783—806).—The method consists in observing the rotatory vibrations of a sphere about its vertical diameter. The paper contains the mathematical treatment of the problem and a full description of the apparatus employed. The value of the coefficient η found by the author for air is 0.0001794 (maximum error 1 per cent.).

J. C. P.

New Method for the Investigation of Gaseous Equilibria at High Temperatures. LEO LÖWENSTEIN (*Zeit. physikal. Chem.*, 1906, **54**, 715—726).—The author describes a method of determining the dissociation of water vapour and hydrogen chloride at high temperatures. The method depends on the fact that glowing platinum acts as a semipermeable membrane, permeable for hydrogen, impermeable for oxygen, chlorine, water vapour, and hydrogen chloride. A closed platinum tube connected with a manometer was placed in an oven through which was passed a slow current of water vapour or hydrogen chloride. The level of the oil in the manometer gradually altered until it became practically steady. From this alteration of level the partial pressure of the free hydrogen outside the platinum tube could be calculated. In this way the author has found the following values for the percentage dissociation of water vapour at various temperatures: 1432°, 0.102 per cent.; 1510°, 0.182 per cent.; 1590°, 0.354 per cent.; 1695°, 0.518 per cent. Hydrogen chloride is found to be dissociated at 1537° to the extent of 0.274 per cent.

J. C. P.

Diffusion of Gases. GEORG KASSNER (*Arch. Pharm.*, 1906, 244, 63—66).—A sample of methane enclosed in a tube between two greased stopcocks had not altered appreciably in composition after two years. Another sample, enclosed in a flask with greased stopper coated with paraffin outside, still contained 95 per cent. of methane after five years. A sample kept over water in an inverted flask only contained 23 per cent. of methane after five years, although 30 cm. of liquid separated the gas from the air; and the volume of the gas had shrunk, corresponding with the smaller solubility of air as compared with methane. A sample enclosed between two greased stopcocks in a tube three-quarters filled with (unboiled) water contained only 84 per cent. of methane after three years. C. F. B.

Relation between the Osmotic Pressure and the Vapour Pressure in a Concentrated Solution. WILL SPENS (*Proc. Roy. Soc.*, 1906, A, 77, 234—240).—A theoretical paper in which the writer arrives at the relationship $Pv_s = sp \log p/p'$, where P is the osmotic pressure, p' the vapour pressure of the solution, p the vapour pressure of the solvent, s the specific volume of the vapour, and v_s is the increment in volume of a large mass of solution when unit mass of the solvent is added. This expression should be compared with the expression $P\mu = sp \log p/p'$ (μ = specific volume of the solvent), deduced by the Earl of Berkeley and Hartley. The two formulæ are identical only when the contraction on dilution is negligible. J. C. P.

Osmotic Pressures of Alcoholic Solutions. PERCIVAL S. BARLOW (*Phil. Mag.*, 1906, [vi], 11, 595—604. Compare Abstr., 1905, ii, 507).—Solutions of various substances in ethyl alcohol showed no osmotic pressure effect when copper ferrocyanide membranes were employed. With a bladder membrane, a pressure was set up in the case of solutions of lithium chloride and camphor, but not in the case of methyl oxalate. When a membrane of gutta-percha tissue was used, lithium chloride solutions exhibited osmotic effects, but the pressures set up were very much smaller than the theoretical values. With increasing concentration, the observed pressures reach a maximum value and then decrease. H. M. D.

Is the Phase Rule Valid in the Case of Colloids? GINO GALEOTTI (*Zeit. physikal. Chem.*, 1906, 54, 727—730. Compare Abstr., 1904, i, 355; 1905, ii, 512).—The author replies in the negative. The condition of a colloidal phase is not defined completely in terms of temperature, pressure, and the masses of the components. Surface tension and electrical state must also be taken into account. J. C. P.

Stratified Structures. RAPHAEL E. LIESEGANG (*Zeit. anorg. Chem.*, 1906, 48, 364—366).—Hausmann (Abstr., 1904, ii, 547) has expressed the opinion that the concentric rings produced when, for instance, silver dichromate is precipitated in a gelatin film can only be obtained with amorphous substances, but the author points out that similar structures can also be observed with crystalline substances.

A mixture of equal volumes of 10 per cent. solutions of gelatin and potassium dichromate was allowed to solidify in a flat dish; a thin strip was then cut out and suspended in such a way that the drying progressed slowly from one end to the other; on subsequent examination, it was found that the salt had been so deposited that layers rich in crystals alternated with others practically free from them.

The author considers that one function of the gelatin in such processes is to hinder the aggregation of the newly-formed molecules to large complexes, but in some cases capillary action probably plays an important part in the phenomenon. G. S.

Polymerisation of Liquids. PETRU BOGDAN (*Ann. sci. Univ. Jassy*, 1906, 3, 223—238).—When the equation of van der Waals is applied to the liquid state, it is found that there are several quantitative discrepancies. For example, the volume at absolute zero is generally about one-quarter instead of one-third of the critical value, the value for PV/T at the critical point is about 22 instead of 30, &c. The author considers that these discrepancies are to be ascribed to association in the liquid state, even in those liquids generally considered as normal. This view is further supported by the fact that for several liquids the value of the molecular weight derived from the molecular surface energy is less than the normal, the constant K being greater than the normal value 2.12. In the author's opinion, therefore, the normal value is obtained with liquids which exhibit polymerisation. At present the values for the association are quite untrustworthy, and very different results are obtained by different methods. The law of Longinescu, $T/cd = n^3$, often leads to values of n which are less than those indicated by the formula of the compound—this again indicating association in the compounds regarded as normal. L. M. J.

Liquid Carbon Dioxide as Solvent. ERNST H. BÜCHNER (*Zeit. physikal. Chem.*, 1906, 54, 665—688. Compare this vol., ii, 71).—Liquid carbon dioxide has in general only a feeble solvent action. Thus, inorganic salts are insoluble, while boric acid, phosphorus pentachloride, arsenic tribromide, antimony tribromide, yellow phosphorus, iodine, and bromine are only slightly soluble. The author has determined the solubility of a large number of liquid and solid organic substances in liquid carbon dioxide, and it appears that these various substances may be put in one of three groups according to their behaviour towards the solvent.

(1) The substance in the liquid condition is miscible in all proportions with liquid carbon dioxide, and the solubility curve runs for the whole of its course underneath the critical line. To this group belong *p*-dichlorobenzene, camphor, carbon disulphide, ether, pentane, amylene, acetylene, benzene, *p*-xylene.

(2) The solubility curve cuts the critical line. Thus there is a saturated solution with a critical temperature in the case of naphthalene, phenanthrene, iodoform, *p*-dibromobenzene, borneol, substituted phenols (except nitrophenol), *p*-chloronitrobenzene, *p*-bromonitrobenzene, 1:2:3- and 1:3:2-dichloronitrobenzenes, phthalic and succinic anhydrides, α -naphthylamine, carbamide, and benzamide. Almost

all inorganic substances, with the exception of gases, belong to this category (compare Smits, Abstr., 1904, ii, 15).

(3) The substance in the liquid condition is not completely miscible with liquid carbon dioxide. In the case of propyl, butyl, and isobutyl alcohols and bromoform, the mutual solubility increases with rising temperature. In the case of urethane, thymol, *o*-nitrophenol, nitrobenzene, the mono- and di-chlorobenzenes not mentioned under (2), and *o*-bromonitrobenzene, the mutual solubility diminishes with rising temperature. In several of the cases just mentioned, a lower critical solution temperature was obtained with super-cooled liquids.

J. C. P.

Anomalous Character of Solubility Curves and the Relation of this to the Formation of Hydrates in Solution. JOHANNES J. VAN LAAR (*Zeit. physikal. Chem.*, 1906, 54, 750—758).—A mathematical paper dealing with a point raised in Roozeboom and Aten's work (Abstr., 1905, ii, 803). The author shows that in dilute saturated solutions hydration must be attributed mainly to the ions if the peculiarities of the solution curve are to be adequately interpreted.

J. C. P.

Properties of Electrically-prepared Colloidal Solutions. E. F. BURTON (*Phil. Mag.*, 1906, [vi], 11, 425—447).—The size of the particles in electrically-prepared colloidal solutions was measured by allowing an intense beam of light, incident at the critical angle, to come to a focus in a thin layer of solution observed through a microscope. When the particles come into the path of the beam, the light is no longer totally reflected, but is scattered into the observing microscope. From the number of bright spots in the field of view, the volume of liquid under observation, and the concentration of the metal in solution, the average diameter of the particles in colloidal solutions of platinum, gold, and silver is found to be $(2-6) \times 10^{-5}$ cm.

The rate of migration of the particles in an electric field was measured under conditions which assured a uniform potential gradient between the electrodes. For platinum, gold, silver, bismuth, lead, and iron, the velocities at 18° for a fall of potential of 1 volt per cm. were found to be 20.3×10^{-5} , 21.6×10^{-5} , 23.6×10^{-5} , 11.0×10^{-5} , 12.0×10^{-5} , and 19.0×10^{-5} cm. per second respectively, the particles of the first three moving towards the positive pole, those of the last three towards the negative pole. Three samples of colloidal silver prepared by using different currents and voltages for sparking, which presumably consisted of particles of different sizes, were found to have the same velocity of migration. The velocity increases with rising temperature and appears to vary inversely as the viscosity of the water. The values of the velocities are of the same order, although somewhat smaller than those of the slowest moving ions, and the author suggests that the charges on the particles result from their interaction with the solvent.

Colloidal solutions of lead, tin, and zinc in methyl and ethyl alcohols and of bismuth, iron, and copper in methyl alcohol were prepared, but solutions of platinum, gold, and silver in the alcohols could not be

obtained. In all these cases, the particles were positively charged. On the other hand, solutions of platinum, gold, and silver in ethyl malonate were readily obtained and the particles were negatively charged. Colloidal solutions could not be obtained with the more electro-positive metals in this solvent. The observed facts indicate that the formation of the solution is essentially dependent on the nature of the metal and of the solvent. The contact differences of potential between the charged particles and the liquid have been calculated.

H. M. D.

Significance of Water in the Formation of Colloidal "Bubbles" from Soaps. FRIEDRICH KRAFFT (*Zeit. physiol. Chem.*, 1906, 47, 5—14. Compare Abstr., 1902, ii, 601).—Observations on the lines of those already recorded (*loc. cit.*) support the view that the molecules in the interior of a mass of water are engaged in a regular vortex movement.

J. C. P.

Filtration of Crystalloids and Colloids through Gelatin. J. A. CRAW (*Proc. Roy. Soc.*, 1906, B, 77, 311—331. Compare Abstr., 1905, ii, 747).—Martin's gelatin filter (a Pasteur-Chamberland filter, the pores of which are filled with solid gelatin) was at first supposed to be permeable to crystalloids and impermeable to colloids, but later work by Waymouth Reid and others showed that this is not strictly true. The author has carried out a series of experiments on this subject with typical colloids and crystalloids as well as with mixtures of these substances.

The filter is highly, but not completely, permeable for such crystalloids as sodium chloride, potassium iodide, and butyric acid; it is only slightly permeable for colloids such as ferric hydroxide and soluble starch. As filtration proceeds, the crystalloids pass through in increasing concentration, whereas the colloids gradually decrease to zero. The presence of one substance often affects the rate of filtration of another, and the permeability also depends on the gelatin; thus a filter prepared with 15 per cent. gelatin solution is less permeable to certain colloids than one of 7.5 per cent., and formalised gelatin is less permeable to sodium chloride than ordinary gelatin. The rate of filtration is greatly dependent on variations in the pressure; thus a sudden diminution gives very concentrated filtrates of both crystalloids and colloids, whereas a gradual diminution has very little effect.

The results with some colloids can be explained on a purely mechanical basis, but with crystalloids, such as sodium chloride, it seems probable that the phenomenon of adsorption plays an important part. The great influence of change of pressure on the permeability seems to depend partly on the diffusion outwards of adsorbed salt from the filter when the pressure is released, and partly on changes in the size of the filter pores.

G. S.

The Periodic System and the Methodical Classification of the Elements. CONSTANTIN ZENGELIS (*Chem. Zeit.*, 1906, 25, 294—295 and 316—317).—The author proposes to modify the periodic classification of the elements so as to reconcile it with the more systematic

arrangement adopted in many text-books for studying the properties of the elements. He accordingly does away with the eighth group, but introduces an additional group comprising the gaseous elements helium, argon, krypton, and xenon before group 1. Elements which have similar properties and have atomic weights differing only by a few units the author considers are not entitled to occupy a separate place in the table, and accordingly the metals iron, cobalt, and nickel are incorporated, together with manganese, in group 7; in the same way, the three elements ruthenium, rhodium, and palladium, and the elements osmium, iridium, platinum, and gold are all placed in group 7. Again, group 3 contains, in addition to the elements ordinarily placed there, two similar aggregations composed respectively of the elements lanthanum, cerium, praseodymium, and neodymium on the eighth horizontal line, and of samarium, gadolinium, terbium, erbium, thulium, and ytterbium on the line below.

P. H.

Pressure Regulator. Temperature Regulator. ANTOINE VILLIERS (*Ann. Chim. anal.*, 1906, 11, 88—90, 90—96).—An apparatus is illustrated for giving a fixed and absolutely constant pressure to a gas evolved under a varying pressure.

The temperature regulator is a modification of the ordinary mercurial regulator, in which the cut off is effected by a disc floating on the top of a column of mercury connected with the reservoir coming into contact with the ground horizontal extremity of the exit tube. The free surface of the mercury being covered by the disc, oxidation is prevented. The papers contain drawings showing the application of the regulators to several purposes.

L. DE K.

Extraction Apparatus. ALLEN ROGERS (*J. Amer. Chem. Soc.*, 1906, 28, 194—196).—An apparatus specially devised for making aqueous extractions of tea, coffee, tanning materials, &c.

It mainly consists of a round-bottomed extractor fitted with a Bunsen valve and connected to two wash-bottles, one of which holds the water, whilst the other serves for collecting the percolate. The water is forced from the bottle into the extractor by applying suction with a filter pump. The water may be brought to the desired temperature by heating the wash-bottles on a water-bath.

L. DE K.

Modified Westphal Balance for Solids and Liquids. F. M. WILLIAMS (*J. Amer. Chem. Soc.*, 1906, 28, 185—187).—Modifications of the Westphal balance are described, which enable it to be used for the determination of the sp. gr. of solids as well as liquids. The modified balance is especially suitable for cements and other solids, the composition of which is changed by immersion in water, and it is also a rapid and accurate instrument for determining the sp. gr. of minerals. The chief modification consists in suspending a special support carrying two pans, one above the other, from the pointer arm at a distance from the fulcrum equal to the length of the other arm. The solid is weighed in the upper pan, the lower pan being immersed

in carbon disulphide or other suitable liquid. The pans are then interchanged, or the object is transferred to the lower pan, and the weighing is repeated. The construction of the instrument is shown by means of diagrams.

E. G.

Inorganic Chemistry.

Oxyhalogen Compounds. IV. Reaction between Chlorine Peroxide and Iodides. WILLIAM BRAY (*Zeit. physikal. Chem.*, 1906, 54, 731—749. Compare this vol., ii, 221—222).—The nature of the reaction between chlorine peroxide and iodide depends on the nature of the medium in which it takes place. In an alkali hydrogen carbonate solution saturated with carbon dioxide, the reaction is represented by the following equation: $\text{ClO}_2 + \text{I}' = \text{ClO}_2' + \text{I} \text{ (a)}$. When the reaction takes place in a so-called "neutral" solution of chlorine peroxide, which, however, contains traces of acid, the action is represented by $3\text{ClO}_2 + 5\text{I}' = 2\text{IO}_3' + 3\text{I} + 3\text{Cl}'$. When, finally, the reaction takes place in an ordinary acid solution, it is represented by $\text{ClO}_2 + 5\text{I}' + 4\text{H}' = 5\text{I} + \text{Cl}' + 2\text{H}_2\text{O}$. The first stage in all cases is probably $2\text{ClO}_2 + \text{I}' + \text{H}_2\text{O} = 2\text{HClO}_2 + \text{IO}'$, which in a hydrogen carbonate solution saturated with carbon dioxide is immediately followed up by $\text{IO}' + \text{I}' + 2\text{H}' = \text{I}_2 + \text{H}_2\text{O}$, giving (a). When a slightly larger trace of acid is present, (a) is followed by $3\text{HClO}_2 + 2\text{I}' = 2\text{IO}_3' + 3\text{HCl}$, the only reaction in which a rapid oxidation of iodide to iodate in an acidified potassium iodide solution takes place.

It has been found that iodine is oxidised to iodate in the following reactions: $\text{ClO}_2 + \text{I} + \text{H}_2\text{O} = \text{HIO}_3 + \text{HCl}$ and $5\text{HClO}_2 + 4\text{I} + 2\text{H}_2\text{O} = 4\text{HIO}_3 + 5\text{HCl}$. It is probable that in these cases it is hypiodous acid and not iodine that is the really active substance.

For the detailed evidence in support of the foregoing equations the original must be consulted. There, too, are described methods for the determination of chlorite in the presence of iodate.

It is noteworthy that the reaction between chlorous acid and an iodide is retarded by increasing the concentration of the iodide and is accelerated by the presence of free iodine. It is probable that chlorous acid does not react primarily with hydriodic acid, or does so very slowly, and that an oxidation of the iodide is induced by a primary reaction between chlorous acid and iodine (or hypiodous acid).

J. C. P.

Electrochemical Equivalent of Iodine. GINO GALLO (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 24—35).—The author has determined the electrochemical equivalent of iodine by electrolysis of a solution of potassium iodide in a specially designed apparatus, the voltage being chosen so that no oxygen was evolved at the anode. The iodine

separating was estimated volumetrically by means of sodium thiosulphate solution, and the silver deposited in a silver voltameter run in series with the potassium iodide cell was also measured. The values obtained in this way for the atomic weight of iodine, compared with $O=16$, vary from 126.82 to 126.98, the mean of the 24 numbers obtained being 126.89. One equivalent of iodine corresponds to 96537 coulombs.

T. H. P.

Change of State of Liquid Sulphur. FRIEDRICH HOFFMANN and R. ROTHE (*Zeit. physikal. Chem.*, 1906, 55, 113—124).—The authors have observed that liquid sulphur about 160° exhibits a behaviour which is probably to be attributed to the transformation of one modification into another (compare Smith and his pupils, *Abstr.*, 1905, ii, 382, 580). When fused sulphur is heated above 160° and is then allowed to cool, not too slowly, it is observed that at about 160° the liquid divides into two layers separated by a meniscus, and thermometric investigation reveals a discontinuity in the cooling curve at this point. If, however, the rate of cooling is diminished, the separation into two phases becomes less distinct and the discontinuity in the cooling curve is less marked. If the rate of cooling is sufficiently slow, neither phenomenon can be observed. Hence, the two modifications must, under ordinary conditions, be completely miscible with each other, and the temperature of 160° cannot be a transition point in the ordinary sense.

J. C. P.

The System Sulphur—Sulphates. KAMILLO BRÜCKNER (*Monatsh.*, 1906, 27, 49—58).—The author has examined the products obtained on heating the anhydrous sulphates of various metals with excess of sulphur. The mixtures were heated in a porcelain crucible, or, when higher temperatures were required, in a hard glass tube through which a current of sulphur vapour was passed.

The sulphates of lithium, sodium, and potassium react at a red heat; sulphur dioxide is evolved and the alkaline residue contains sulphide, thiosulphate, and polysulphide. The sulphates of the alkaline earth metals yield similar products, but react less readily. Magnesium, glucinum, and aluminium do not react at a red heat. Chromic sulphate gives a black sulphide insoluble in hot concentrated hydrochloric acid, cerium sulphate a reddish-brown sulphide decomposed by hydrochloric acid, and uranyl sulphate a mixture of uranous oxide and uranoso-uranic oxide. The sulphates of manganese, zinc, cadmium, iron (ferrous and ferric), nickel, copper, lead, mercury, thallium, silver, and cobalt are converted into sulphides with evolution of sulphur dioxide. Bismuth and antimony sulphates yield bluish-grey sulphides of metallic appearance, but in the case of bismuth, the metal is obtained when a smaller proportion of sulphur is employed.

The mode of formation of the various products is discussed.

H. M. D.

Selenium obtained with Organic Reducing Agents. WILLIAM OECHSNER DE CONINCK and CHAUVENET (*Bull. Acad. Roy. Belg.*, 1906, 601—603).—When selenic acid is heated with formic,

oxalic, malonic, or pyruvic acid, paraldehyde, formaldehyde, trioxymethylene, ænanthaldehyde, benzaldehyde [dissolved in alcohol], or with an aqueous solution of dextrose or lævulose, it is reduced to selenium. Neither succinic nor acetic acid reduces selenic acid.

T. A. H.

Behaviour of Selenium towards Light and Temperature.

II. ROBERT MARC (*Zeit. anorg. Chem.*, 1906, 48, 393—426).—A more detailed account of work already published (this vol., ii, 226).

G. S.

Selenium Dioxide. WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1906, 142, 571—573).—One part of selenium dioxide dissolves in 2·67, 2·6, and 2·54 parts of water at 11·3°, 14°, and 15·6° respectively; in 9·84 parts of alcohol (93°) at 14°, in 15 parts of methyl alcohol at 11·8°, in 23 parts of crude acetone at 15·3°, and in 90 parts of acetic acid at 12·9°. The specific gravities of 1—10 per cent. solutions of selenium dioxide in water are tabulated in the original. Reddish-brown amorphous selenium, insoluble in carbon disulphide, separates slowly when aqueous solutions of the dioxide are exposed to light.

Selenium dioxide is converted by nitric acid into selenic acid, by hot sulphuric acid into selenium sulphoxide, SeSO_3 , hydrogen selenide, and some amorphous, reddish-brown selenium; by phosphorus pentachloride into selenium tetrachloride, and by phosphorus trichloride into brown, amorphous selenium. Phosphorus oxychloride is formed in the last two reactions. With hydrazine, the dioxide yields nitrogen and black, amorphous selenium, and when warmed with hydroxylamine hydrochloride, nitrogen is evolved and reddish-brown, amorphous selenium separates.

T. A. H.

Action of Nitrogen Peroxide on Ammonia and on Some Ammonium Salts. ADOLPHE BESSON and GEORGES ROSSET (*Compt. rend.*, 1906, 142, 633—634).—Liquid ammonia reacts explosively with solid nitrogen peroxide at -80° , but if a current of gaseous ammonia at -20° is passed over the peroxide, the reaction is moderated and the products are nitrogen, nitric oxide, water, ammonium nitrate, and a trace of ammonium nitrite. Nitrogen peroxide reacts slowly with ammonium chloride in the cold; the reaction is, however, complete in sealed tubes at 100° with the formation of chlorine, nitrogen, nitrous oxide, nitrogen trioxide, nitrosyl chloride, water, and nitric acid. When ammonium nitrate or sulphate replace the chloride in the above reaction, the products are nitrogen and nitric acid or nitrogen, and a mixture of nitric and sulphuric acids respectively.

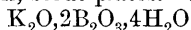
M. A. W.

An Instance of Choke Damp free from Carbon Dioxide. BERTRAM BLOUNT (*J. Hygiene*, 1906, 6, 175—178).—"Choke damp" or "black damp" in mines and wells is air deficient in oxygen and rich in carbon dioxide. Very few cases of deficiency in the latter gas have been described. In the present instance it was noticed that

candles would not burn in a room used for cold storage. On analysis, the air was found to contain 17.6 per cent. of oxygen, and the remainder inert gas (nitrogen, argon, &c.). This would account for the extinction of a light, but the amount of oxygen was sufficient not to endanger the lives of workers there, who apparently suffered no inconvenience. The amount of carbon dioxide was negligible and can be accounted for by the presence of workmen. The gas came from a disused well shaft in communication with the room. The clay through which the shaft passed contained iron pyrites, which accounted for the loss of oxygen. Either no carbon dioxide was formed from the carbonates of the clay, or, if any was formed, it must have been subsequently absorbed by the mud and water. W. D. H.

Borates of the Alkali Metals and of Ammonium. ALBERT ATTERBERG (*Zeit. anorg. Chem.*, 1906, 48, 367—373).—The work described in this communication was carried out more than thirty years ago, and the author has been induced to publish it in accessible form by the appearance of Auerbach's recent paper (*Abstr.*, 1904, ii, 118) on the same subject. Only mono-, di-, and penta-borates of the metals above mentioned could be obtained; they all melt to clear glasses at a high temperature.

Potassium monoborate, $K_2O, B_2O_3, 3H_2O$, separates from a strongly alkaline solution in small, stout plates. *Potassium diborates*:



occurs in lustrous, six-sided prisms; $K_2O, 2B_2O_3, 5\frac{1}{2}H_2O$ forms short, hexagonal prisms; $K_2O, 2B_2O_3, 6H_2O$ occurs in short, monoclinic prisms. *Potassium pentaborate*, $K_2O, 5B_2O_3, 8H_2O$, crystallises in rhombic octahedra.

Sodium monoborates: $Na_2O, B_2O_3, 4\frac{1}{2}H_2O$ forms four-sided prisms; $Na_2O, B_2O_3, 5\frac{1}{2}H_2O$, long prisms; $Na_2O, B_2O_3, 8H_2O$ forms small, six-sided crystals. *Sodium diborates*: $Na_2O, 2B_2O_3, 5H_2O$, octahedral borax; $Na_2O, 2B_2O_3, 10H_2O$, ordinary prismatic borax. *Sodium pentaborate*, $Na_2O, 5B_2O_3, 10H_2O$, obtained in the form of prismatic crystals, is partially hydrolysed in aqueous solution.

Ammonium diborate, $(NH_4)_2O, 2B_2O_3, 5H_2O$, occurs in tetragonal pyramids; *ammonium pentaborate*, $(NH_4)_2O, 5B_2O_3, 8H_2O$, in rhombic double pyramids.

Barium monoborates: $BaO, B_2O_3, 2H_2O$, a crystalline powder; $BaO, B_2O_3, 4H_2O$, short, four-sided prisms. *Barium sesquiborate*, $2BaO, 3B_2O_3, 7H_2O$, was obtained by interaction of boric acid and excess of barium hydroxide as a voluminous, amorphous precipitate.

G. S.

Hydrates of Sodium Thiosulphate. STEWART W. YOUNG and W. E. BURKE (*J. Amer. Chem. Soc.*, 1906, 28, 315—347. Compare *Abstr.*, 1905, ii, 32, and Young and Mitchell, *Abstr.*, 1905, ii, 31).—An account is given of twelve crystalline hydrates of sodium thiosulphate and the anhydrous salt. The methods of preparing the various hydrates are described, and the solubility of each has been determined at intervals of 5°, from 0° upwards. Transition points have been determined from the intersections of the solubility curves and in many

cases have also been measured directly. A number of observations has been made with reference to super-cooling and super-heating of the different forms, and it is shown that super-heating is as common in this system as super-cooling and that both probably occur in the neighbourhood of every transition point; both phenomena are probably transitory.

The hydrates are classified in groups on the basis of their behaviour in undergoing transition with rising temperature, and are accordingly termed primary, secondary, tertiary, &c. The following is a list of the hydrates with their transition and melting points. Primary pentahydrate (formerly called α -pentahydrate), m. p. $48\cdot45^\circ$, transition point into the primary dihydrate, $48\cdot17^\circ$. Primary dihydrate (α -dihydrate), transition point into the anhydride, $66\cdot5^\circ$. Secondary pentahydrate (β -pentahydrate), transition point into the secondary tetrahydrate, $30\cdot22^\circ$. Secondary tetrahydrate (originally known as the d -form), m. p. $41\cdot65^\circ$, transition point into the secondary monohydrate, $40\cdot65^\circ$. Secondary monohydrate (α -monohydrate), transition point into the anhydride, $56\cdot5^\circ$. Tertiary hexahydrate, which also acts as a quaternary form and was formerly regarded as γ -pentahydrate, m. p. $14\cdot35^\circ$, transition point into the quaternary $4/3$ -hydrate, $14\cdot3^\circ$, and into the tertiary sesquihydrate, $14\cdot25^\circ$. Tertiary sesquihydrate, transition point into the tertiary monohydrate, $48\cdot5^\circ$. Tertiary monohydrate (β -monohydrate), transition point into the anhydride, 61° . Quaternary $4/3$ -hydrate, $3\text{Na}_2\text{S}_2\text{O}_3\cdot4\text{H}_2\text{O}$, originally called the c -form, transition point into the anhydride, 58° . Quintary dihydrate (β -dihydrate), transition point into the quintary monohydrate, $27\cdot5^\circ$. Quintary monohydrate (γ -monohydrate), transition point into the quintary hemihydrate, 43° . Quintary hemihydrate, transition point into the anhydride, 70° .

The paper is illustrated with curves and diagrams.

E. G.

Presence of Chlorate in Sodium Nitrate. LÉON GRIMBERT (*J. Pharm. Chim.*, 1906, [vi], 23, 98—100).—Small quantities of chlorate were found in three samples of commercial sodium nitrate. It is pointed out that this impurity should be guarded against when sodium nitrate is employed in destroying organic matter as a preliminary to the estimation of chlorine in organic products.

T. A. H.

Density of Solutions of Sodium Carbonate and Sodium Hydroxide. II. RUDOLF WEGSCHEIDER (*Monatsh.*, 1906, 27, 13—30. Compare Abstr., 1905, ii, 521).—The interpolation formulæ previously given for the densities of solutions of sodium carbonate and sodium hydroxide were deduced on the false assumption that Lunge's data represent density values referred to water at 4° . The formulæ are now corrected.

H. M. D.

Preparation of Metallic Lithium. OTTO RUFF and OTTO JOHANNSEN (*Zeit. Elektrochem.*, 1906, 12, 186—188).—The electrolysis of mixtures of lithium salts with salts of the other alkali metals always yields impure lithium; the electrolysis of pure lithium chloride is inconvenient on account of the volatility and high resistance of this salt;

the addition of lithium fluoride increases the resistance. The best electrolyte is a mixture of lithium bromide with 13 per cent. of lithium chloride; this is the mixture of lowest melting point (520°), pure lithium chloride and bromide melting at 606° and 546° respectively. With this mixture and using a carbon anode and iron cathode a current of 100 amperes can be maintained with an *E.M.F.* of 10 volts. The current efficiency is about 80 per cent. The metal contained 0.17 per cent. of sodium, but was otherwise pure; its melting point was 180° (corr.). T. E.

Sulphides of Rubidium and Cæsium. WILHELM BILTZ and ERNST WILKE-DÖRFURT (*Zeit. anorg. Chem.*, 1906, 48, 297—318).—In a former paper (Abstr., 1905, ii, 162), the preparation of the pentasulphides of these two metals has been described; in the present communication, an account of the other sulphides is given.

Rubidium monosulphide, $\text{Rb}_2\text{S}_4\cdot 4\text{H}_2\text{O}$, and the corresponding *cæsium* salt, $\text{Cs}_2\text{S}_4\cdot 4\text{H}_2\text{O}$, are obtained in colourless, deliquescent crystals on allowing the concentrated aqueous solutions to remain for some time in a desiccator over calcium chloride. The *hydrosulphides*, RbSH and CsSH , obtained in a similar manner from the aqueous solutions, also occur in colourless, deliquescent crystals. Anhydrous monosulphides could not be obtained.

Rubidium tetrasulphide, $\text{Rb}_2\text{S}_4\cdot 2\text{H}_2\text{O}$, was obtained from an aqueous solution containing calculated amounts of the monosulphide and sulphur; it forms small, prismatic, yellow crystals which dissolve unchanged in water, but undergo decomposition on dehydration. *Cæsium tetrasulphide*, Cs_2S_4 , prepared in an analogous manner, forms reddish-yellow prisms, soluble in water without decomposition. No other sulphides of uniform composition could be isolated from monosulphide solutions containing varying proportions of dissolved sulphur, but *disulphides* are apparently obtainable on heating the pentasulphides for some time in a current of hydrogen at $700\text{--}800^{\circ}$.

With the object of determining in a more definite way what sulphides of these metals exist, freezing-point curves of the systems were constructed. In the case of rubidium, the curve starting from the disulphide shows one distinct maximum at a point corresponding with the composition of the pentasulphide, as well as four eutectic points; from the shape of the curve, the conclusion is drawn that tri-, tetra-, and hexa-sulphides also exist; unlike the pentasulphide, they dissociate into their components at temperatures below their melting points. The curve of the system cæsium—sulphur indicates the existence of the same sulphides as in the case of rubidium, but both the penta- and hexa-sulphides give distinct maxima. No indication of the existence of other sulphides than those referred to has been obtained. G. S.

Silver and Arsenic. K. FRIEDRICH and A. LEROUX (*Metallurgie*, 1906, 3, 192—195).—The freezing-point curve for alloys containing from 0 to 19 per cent. of arsenic has been determined, and shows only a descending branch, corresponding with the separation of silver crystals. The eutectic horizontal is at 527° , and is unbroken. Within the limits examined, there is no evidence of the existence of a compound of silver

and arsenic, and the existence of a compound Ag_3As (Descamps, Abstr., 1878, 705) is disproved. Microscopic sections show only silver and the eutectic.

Alloys of the same character, containing 87.2—89.5 per cent. of arsenic, are obtained on reducing silver arsenate with potassium cyanide at a low temperature. C. H. D.

Silver-zinc Alloys. G. I. PETRENKO (*Zeit. anorg. Chem.*, 1906, 48, 347—363. Compare Heycock and Neville, Trans., 1897, 71, 417; Herschkowitsch, Abstr., 1898, ii, 582).—The investigation was carried out by Tammann's method of thermal analysis, and the results were controlled by microscopic observations. The observed temperatures of initial crystallisation agree very closely with those obtained by Heycock and Neville.

There are five breaks in the freezing-point curve, at 28.1, 37.7, 47.6, 60, and 95 per cent. by weight of zinc, the first four of which correspond with the compounds Ag_3Zn_2 , AgZn , Ag_2Zn_3 , and Ag_2Zn_5 respectively. The compound AgZn forms complete series of mixed crystals with the compounds Ag_3Zn_3 and Ag_3Zn_2 ; on the other hand, the compounds Ag_2Zn_3 and Ag_2Zn_5 have only a limited mutual solubility, which is also true of the latter compound and zinc, so that there are breaks in the series of mixed crystals. Within certain limits, the structure of the alloys depends on the velocity of cooling, thus, when the compound Ag_3Zn_2 is allowed to cool slowly below 640° , it decomposes into AgZn and a saturated mixed crystal. The compound AgZn exists in two forms which have a transition point at 260° .

The hardness of these alloys reaches its maximum between 47.6 and 60 per cent. by weight of zinc, and the brittleness is also greatest between these limits; the degree of hardness does not depend on the rate of cooling.

Photo-micrographs of several of the alloys are given in the paper.

G. S.

Silver Oxide and Silver Suboxide. GILBERT N. LEWIS (*J. Amer. Chem. Soc.*, 1906, 28, 139—158. Compare Abstr., 1905, ii, 578).—Guntz (Abstr., 1899, ii, 418) has described experiments from which he concluded that when silver oxide is heated in a closed tube at 358° , it decomposes into the suboxide and oxygen, and that the suboxide then suffers partial decomposition until equilibrium is attained. It is now shown that silver suboxide is not produced under these conditions, and that Guntz's results are capable of a different interpretation.

The decomposition pressure of silver oxide has been determined at 302° , 325° , and 445° , and the results show that the equilibrium pressures in the system, silver oxide, silver, oxygen, are approximately 20.5, 32, and 207 atmospheres respectively at these temperatures. Silver suboxide was not produced in any of the experiments, and is probably incapable of existence at these temperatures. From the change of equilibrium pressure with the temperature, the heat of formation of silver oxide has been calculated and found to be 6.4 Cal. It is shown that the average of five determinations of this quantity based on the available calorimetric data is 6.34 Cal., and it is therefore

concluded that the silver oxide which exists between 302° and 445° is, from a thermodynamical point of view, identical with that existing at the ordinary temperature. The decomposition pressure of silver oxide at 25° has been calculated and found to be 5×10^{-4} atmospheres.

E. G

Alloys of Calcium. L. STOCKEM (*Metallurgie*, 1906, 3, 147—149. Compare Quasebart, this vol., ii, 229).—Calcium dissolves in molten cast iron with great development of heat, but when large quantities are used the metal is rapidly coated with a crust of calcium carbide which prevents further action. Some calcium carbide always remains mechanically entangled in the iron. Ferric oxide reacts vigorously with an excess of metallic calcium; the iron formed is pure and ductile, and does not contain a trace of calcium.

Calcium alloys with copper in all proportions. The products are brittle, an alloy containing 20 per cent. of calcium being pure white and crumbling on exposure to air. Copper-calcium may be advantageously employed in place of phosphor-copper for deoxidising copper.

Aluminium and magnesium also alloy with calcium in all proportions. When 10 per cent. of calcium is present, the alloys are so brittle as to be easily powdered in a mortar.

C. H. D.

Hydration of Portland Cement. PAUL ROHLAND (*Zeit. angew. Chem.*, 1906, 19, 327—331. Compare Abstr., 1905, ii, 319).—A study of the influence of a number of different salts on the rate of hydration of Portland cement has shown that sodium carbonate and aluminium salts increase the rate of hydration; moreover, the increase produced by pairs of salts such as sodium carbonate and aluminium chloride or aluminium sulphate and chloride acting together is considerably greater than would be expected from a summation of their individual effects. On the other hand, when two salts such as potassium dichromate and borax, each of which taken alone produces a retarding influence, are allowed to act together, the retardation is less than can be accounted for by adding together the effects due to each one separately. The paper is brought to a close with a theoretical discussion regarding the mechanism of the influence of these various salts, for details of which the original should be consulted.

P. H.

Combustion of Cadmium. WILHELM MANCHOT (*Ber.*, 1906, 39, 1170—1171).—When cadmium is burnt at as low a temperature as possible, the smoke, which consists mainly of cadmium oxide, contains also some cadmium peroxide.

W. A. D.

Oxides of Thallium. I. OTTO RABE (*Zeit. anorg. Chem.*, 1906, 48, 427—440).—When an alkaline solution of a thallic salt is treated with a 3—5 per cent. solution of hydrogen peroxide, anhydrous thallic oxide, Tl_2O_3 , separates as a dark brown, flocculent precipitate which slowly changes to small, lustrous crystals of chocolate-brown colour. If precautions are taken to keep the temperature low and the peroxide is used in excess, the yield is almost quantitative; the excess of hydrogen peroxide undergoes decomposition in a catalytic manner

without affecting the thallic oxide. When, on the other hand, the experiment is carried out at 80—100° in strongly alkaline solution (10—35 per cent. of potassium hydroxide), a black modification of the same oxide is obtained as a heavy, sandy, practically anhydrous powder.

The brown oxide is easily, the black much less readily, soluble in dilute mineral acids; in both cases the process is accompanied by slight reduction to thalious salt. The brown oxide also undergoes partial reduction on boiling with water, whilst the black oxide is scarcely affected. The specific gravities were determined with the pyknometer by displacement of xylene, and are, for the brown modification 9.65 at 21°, for the black 10.19 at 22°. G. S.

Decomposition of an Aqueous Solution of Copper Sulphate by Aluminium Alloys. HECTOR PÉCHEUX (*Compt. rend.*, 1906, 142, 575—577. Compare Abstr., 1905, ii, 526).—Quantitative investigation of the reactions resulting in the evolution of hydrogen and precipitation of copper, which take place when a bismuth-aluminium alloy containing 94 per cent. of the latter metal is placed in an aqueous solution of copper sulphate, showed that these may be represented by the equations $\text{Al}_2 + 6\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} + 3\text{H}_2$; $\text{H}_2 + \text{CuSO}_4 = \text{H}_2\text{SO}_4 + \text{Cu}$, and $3\text{CuSO}_4 + \text{Bi}_2 = \text{Bi}_2(\text{SO}_4)_3 + 3\text{Cu}$. With a magnesium-aluminium alloy, on the contrary, the whole of the hydrogen produced by the action of the magnesium on the water is evolved, and the copper precipitated is solely the result of the action of the aluminium on the copper sulphate, thus: $3\text{Mg} + 6\text{H}_2\text{O} = 3\text{Mg}(\text{HO})_2 + 3\text{H}_2$ and $3\text{CuSO}_4 + \text{Al}_2 = \text{Al}_2(\text{SO}_4)_3 + 3\text{Cu}$. With a tin-aluminium alloy, hydrogen is evolved and metallic copper is precipitated, but the reaction soon stops owing to the formation on the surface of the alloy of an insoluble layer of alumina. In all three cases, the alloys used were previously filed to produce roughened surfaces. A polished and re-heated fragment of the magnesium-aluminium alloy, when immersed in the copper sulphate solution, acquired after ten hours a hard coat of copper which could readily be separated as a coherent film (0.09 mm. thick) with a knife blade. T. A. H.

Calcium and Strontium Mercuric Iodides. ANDRÉ DUBOIN (*Compt. rend.*, 1906, 142, 573—574).—*Calcium mercuric iodide*, $\text{CaI}_2 \cdot \text{HgI}_2 \cdot 8\text{H}_2\text{O}$, obtained by slow evaporation at atmospheric temperature of a solution containing calcium 3.97, mercury 21.84, iodine 52.8, and water 21.39 per cent., crystallises in transparent needles 5 cm. long and has a sp. gr. 3.25 at 0°.

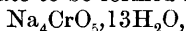
Strontium mercuric iodide, $\text{SrI}_2 \cdot 5\text{HgI}_2 \cdot 8\text{H}_2\text{O}$, was obtained in small crystals, together with mercuric iodide, by slightly cooling a solution (sp. gr. 2.5 at 16.5°) containing strontium 7.12, mercury 20.4, iodine 45.63, and water 26.85 per cent. When strongly cooled, the solution deposits the same salt in iridescent lamellæ, having a sp. gr. 4.66. This strontium salt may also be obtained in larger quantity by saturating the solution with mercuric iodide at 70° and allowing the liquid to cool.

A second *strontium mercuric iodide* [$\text{SrI}_2 \cdot \text{HgI}_2 \cdot 8\text{H}_2\text{O}$] was obtained in long prisms, having a sp. gr. 3.22 to 3.36, by slowly evaporating a

liquid having the composition strontium 7.85, mercury 21.22, iodine 50.44, and water 20.49 per cent. T. A. H.

Action of Silicon Tetrachloride on Cobalt. ÉMILE VIGOUROUX (*Compt. rend.*, 1906, 142, 635—637. Compare this vol., ii, 32).—Silicon tetrachloride is reduced by cobalt at the temperature of the electric furnace with the formation of cobalt chloride, which is volatile, and a residue of a cobalt silicide. At 1200° to 1300°, the reaction is complete, and ceases when the cobalt is converted into the silicide, Co_2Si (compare Abstr., 1896, ii, 176; Lebeau, Abstr., 1903, ii, 80), which has a sp. gr. 7.28 at 0° and differs from the corresponding iron silicide in that it is not attracted by a magnet (compare Moissan, Abstr., 1896, ii, 173). M. A. W.

Alkali Chromates. FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1906, 55, 71—98).—The bulk of this work has been already reported (Abstr., 1905, ii, 818, 820; this vol., ii, 24). The various equilibria at 30° in the system $\text{Na}_2\text{O} + \text{CrO}_3 + \text{H}_2\text{O}$ have also been studied, and the results are now communicated. The solid phases which at one concentration or another are in equilibrium with the solution are: $\text{NaOH}, \text{H}_2\text{O}$; Na_2CrO_4 ; $\text{Na}_4\text{CrO}_5, 13\text{H}_2\text{O}$; $\text{Na}_2\text{CrO}_4, 4\text{H}_2\text{O}$; $\text{Na}_2\text{Cr}_2\text{O}_7, 2\text{H}_2\text{O}$; $\text{Na}_2\text{Cr}_3\text{O}_{10}, \text{H}_2\text{O}$; $\text{Na}_2\text{Cr}_4\text{O}_{13}, 4\text{H}_2\text{O}$, and CrO_3 . All these sodium chromates are soluble in water without decomposition. An interesting point brought out by the author's work, and made evident in the triangular diagram usually employed, is the following. When chromium trioxide is added to a saturated solution of sodium hydroxide, the first chromate to be formed is Na_2CrO_4 , not



as might be expected. Further addition of chromium trioxide is necessary to convert Na_2CrO_4 into $\text{Na}_4\text{CrO}_5, 13\text{H}_2\text{O}$. That is to say, one chromate is converted by addition of chromium trioxide into another chromate which contains less chromium than the first. This is possible only because of the high percentage of water contained in the second chromate. J. C. P.

Gold-zinc Alloys. RUDOLF VOGEL (*Zeit. anorg. Chem.*, 1906, 48, 319—332. Compare Heycock and Neville, Trans., 1897, 71, 419).—The complete freezing-point curve of the system has been constructed and the conclusions arrived at by Tammann's method of thermal analysis have been confirmed by microscopic observations and by chemical analysis.

The freezing-point curve shows a eutectic point at 14 per cent. by weight of zinc, a distinct maximum at 25 per cent., and three breaks at 33, 77, and 88.5 per cent. of zinc respectively. The maximum corresponds with a compound of the formula AuZn , and besides this two other compounds exist, the respective formulæ and composition of which are: Au_3Zn_5 , 35.6 per cent. of zinc, and AuZn_8 , 72.6 per cent. of zinc. It is remarkable that the composition of none of the compounds corresponds with the ordinary valencies of the component elements.

From 0—12.5 per cent. by weight of zinc, mixed crystals separate

out; from 12.5—16 per cent., the primary separation of the saturated crystals is followed by the appearance of a eutectic, the second component of which is a new series of mixed crystals containing the compound AuZn ; from 16—25 per cent. of zinc, the new series separates alone. From 25—31 per cent., a third series of mixed crystals separates; from 31—35.6 per cent., the primary separation of the latter is followed by the appearance of the compound Au_3Zn_5 . The latter compound enters into a fourth series of mixed crystals from 35.6—61 per cent. of zinc; from the latter point to 72.6 per cent., the primary separation of these crystals is followed by the appearance of the compound AuZn_8 , beyond which point no mixed crystals are formed.

The alloys rich in gold have about the same hardness as the latter, but are not quite so tenacious. Between 31 and 61 per cent. of zinc, they are extremely hard and brittle, due to the compound Au_3Zn_5 ; above the latter point, the hardness and brittleness gradually diminish.

G. S.

Gold-cadmium Alloys. RUDOLF VOGEL (*Zeit. anorg. Chem.*, 1906, **48**, 333—346. Compare Heycock and Neville, *Trans.*, 1892, **61**, 883, and preceding abstract).—The freezing-point curve of the system shows two breaks at 623° and 30 per cent. and 493° and 63 per cent. by weight of cadmium respectively, and a eutectic point at 303° and 87 per cent. of the same metal. The first break corresponds with a compound of the formula Au_4Cd_3 , the second with a compound AuCd_3 .

From 0—18 per cent. by weight of cadmium, mixed crystals separate; at the latter point they are saturated, and from 18—30 per cent. the primary separation of the saturated mixed crystals is followed by the separation of the compound Au_4Cd_3 ; from 30—51 per cent., a second series of mixed crystals appears, and from 51—63 per cent. the separation of these crystals is followed by the appearance of the compound AuCd_3 ; beyond this point no mixed crystals form, the components of the eutectic mixture at 87 per cent. being the compound AuCd_3 and cadmium.

Heycock and Neville (*loc. cit.*), by distilling off the excess of cadmium from an alloy of the two metals, obtained a residue which corresponded approximately with the composition CdAu , and considered the existence of a compound of this formula as proved, but the author points out that this method of procedure is only applicable when the vapour pressure of the volatile metal alters in a discontinuous way at a point corresponding with the composition of the compound, a condition which is not fulfilled when, as in this case, mixed crystals with the volatile component are formed.

The hardness reaches its maximum in the alloys containing 18—30 per cent. and 51—63 per cent. of cadmium respectively; the remaining alloys have about the same degree of hardness as the metals themselves. Some of the alloys are extremely brittle; this property attains its maximum at 51—63 per cent. of cadmium.

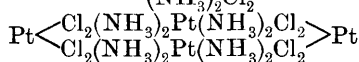
Photo-micrographs of several of the alloys are given in the paper.

G. S.

Action of Hot Sulphuric Acid on Platinum and Iridium Salts in the Presence of Ammonium Sulphate. MARCEL DELÉPINE (*Compt. rend.*, 1906, 142, 631—633. Compare this vol., ii, 24, 93).—A platinum-iridium alloy containing 10 per cent. of the latter metal is dissolved to the extent of 0.10 gram per hour per square decimetre by sulphuric acid at 365°. On boiling the solution with ammonium sulphate, the platinum is deposited in the spongy form, and the residual solution exhibits the beautiful green colour changing to a deep violet on the addition of nitric acid which is a characteristic reaction of iridium salts. From the green solution, the author has isolated three ammonium iridosulphates: a greenish-blue salt which gives a blue precipitate with barium or strontium salts and is slowly decomposed by ammonia; a green salt which gives no precipitate with neutral barium chloride, but a greenish-brown precipitate with the reagent in the presence of alkalis; and an olive-brown salt which gives no precipitate with neutral barium chloride, and a brown precipitate in the presence of ammonia. M. A. W.

A New Red Compound Isomeric with Magnus' Green Salt. SOFUS M. JÖRGENSEN and SÖREN P. L. SÖRENSEN (*Zeit. anorg. Chem.*, 1906, 48, 441—445).—Magnus' green salt is usually obtained by the action of potassium platinous chloride on platodiammine chloride, $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$, in aqueous solution, but the authors have observed that in certain circumstances the same substances interact with formation of an isomeric red salt. The conditions favourable for the production of the latter are absence of potassium platinichloride (traces of which are often present in the platinous salt) and very dilute neutral or slightly ammoniacal solution. The precipitate is washed with aqueous and finally with absolute alcohol, and forms small, ill-defined needles, rose-red in colour. The same salt is obtained in well-defined, small, tetragonal prisms by interaction of the yellow plato-dimethylamine-ammine platinous chloride (compare this vol., i, 338) with platodiammine chloride in the presence of a large excess of water.

The red salt is anhydrous, and in the dry condition is very stable, but on boiling with water it is changed quantitatively into the green salt; the converse change has not been observed. Both salts contain the residues $\text{Pt}''(\text{NH}_3)_4$ and $\text{Pt}''\text{Cl}_4$, and the authors consider it probable that the formulæ $\text{Pt} \left\langle \begin{smallmatrix} (\text{NH}_3)_2\text{Cl}_2 \\ (\text{NH}_3)_2\text{Cl}_2 \end{smallmatrix} \right\rangle \text{Pt}$ and



are to be ascribed to the red and green salts respectively. G. S.

Colloidal Nature of the Black Palladium Solution obtained by means of Carbon Monoxide. JULIUS DONAU (*Monatsh.*, 1906, 27, 71—74. Compare Abstr., 1905, ii, 462).—The blackish-brown solution obtained by passing carbon monoxide into an aqueous solution of palladous chloride containing 0.005—0.05 per cent. of palladium has the same colour as has the palladium borax bead (Abstr., 1904, ii, 784) and Bredig's colloidal palladium solution, obtained by the disintegrating action of an electric discharge (Abstr., 1900, ii, 213). For

the preparation of the solution, conductivity water is less suitable than ordinary distilled water; when the reduction, which takes place more quickly than that of auric chloride, is complete, the conductivity of the solution becomes constant.

The filtrate obtained on precipitation of the metal with hydrochloric acid contains no palladium. Solutions containing 0.01 per cent. or more of palladium gradually deposit a part of the metal as a black precipitate; when evaporated, the solution darkens, and finally the metal is precipitated. The hydrochloric acid cannot be removed from the solution by dialysis; on prolonged dialysis, the palladium is partially precipitated, whereas the solution passes through a porous cell almost unchanged. The metal is precipitated also when the liquid hydrosol is shaken with animal charcoal or barium sulphate, or an electrolyte is added. These precipitations are diminished or prevented by the presence of a protecting agent, such as gum arabic or gelatin.

When an electric current is passed through the liquid hydrosol in a U-tube, the cathode limb becomes almost colourless, and has the conductivity only of highly purified water; the anode limb appears almost black, and a sharp line of demarcation between the two portions of the solution is observed. The hydrosol gradually dissolves at the anode, forming palladous chloride, when the metallic ion is deposited at the cathode.

G. Y.

Mineralogical Chemistry.

Occurrence of Sulphur and Celestite at Maybee, Michigan.
E. HENRY KRAUS and W. F. HUNT (*Amer. J. Sci.*, 1906, [iv], 21, 237—244).—The beds of dolomite-rock exposed in the Woolmish quarry, near Maybee, in Monroe Co., Michigan, are compact in the upper layers, but porous and cavernous in the lower layers. In the latter, waters containing hydrogen sulphide are encountered, and the cavities are lined with crystals of native sulphur, celestite, calcite, and sometimes gypsum. The compact rock is impregnated with a considerable amount of strontium sulphate, and varies in sp. gr. from 2.80 to 3.45. Analysis (I) of a sample showed it to be a normal dolomite containing 14.32 per cent. of celestite. Analysis (II) of the cavernous rock also indicates a normal dolomite with much silica and bituminous matter. When treated with hydrochloric acid, the cavernous rock gives off hydrogen sulphide, and the numbers in the analysis also indicate that some of the strontium is present as sulphide. This strontium sulphide has probably been formed from the celestite by the reducing action of the organic matter contained in the rock, and its presence would account for the occurrence of the sulphuretted waters and the native sulphur.

	SiO ₂ .	Al ₂ O ₃ , Fe ₂ O ₃ .	CaO.	MgO.	BaO.	SrO.	SO ₃ .	CO ₂ .
I.	0·58	0·37	25·18	18·11	0·13	7·86	6·33	39·55
II.	20·14	0·86	19·56	15·32	0·07	0·66	0·56	21·94
III.*	0·22	0·14	0·46	0·13	1·29	53·76	43·59	—

	Na ₂ O.	K ₂ O.	P ₂ O ₅ .	Cl.	S.	H ₂ S.	Organic matter.	Total.
I.	0·11	0·05	0·02	0·04	—	trace	0·92	99·25
II.	0·09	0·07	—	0·03	0·02	—	10·72	100·00

* Total of III, 99·59.

Analysis III is of clear, transparent crystals of celestite with a slight blue tint and sp. gr. 3·979. A crystallographic description is given of the material, and natural etched figures on faces of celestite crystals are figured.

L. J. S.

Physiological Chemistry.

Post-mortem Changes in the Blood. P. MORAWITZ (*Beitr. chem. Physiol. Path.*, 1906, 8, 1—14).—The blood removed from human corpses twelve to twenty-four hours after death was examined. After many diseases, the blood is uncoagulated; this depends on lack of fibrinogen. The disappearance of fibrinogen is due to fibrinolysis, the rate of which varies, but may be so great that within ten hours after death all the fibrin and fibrinogen have disappeared. The destruction of fibrinogen can be observed before coagulation sets in. The other proteids of the blood are not attacked by the fibrinolytic ferment. In many cases, the blood resembles that which may be artificially produced by poisoning with phosphorus. If the blood contains fibrinogen, it coagulates slowly; this depends on paucity in thrombokinase. As a rule, fibrin-ferment is only present in small quantities. No definite statement can be made on the occurrence of substances which inhibit coagulation. W. D. H.

Influence of Calcium Salts on the Heat-coagulation of Fibrinogen and other Proteids. CHARLES MURRAY (*Bio-chem. J.*, 1906, 1, 167—174).—Decalcification of blood-plasma, hydrocele fluid, &c., by oxalate, citrate, or fluoride, lowers the heat-coagulation point of fibrinogen from 56° to about 50°. Doubling or trebling the amount of decalcifying agent added makes no appreciable difference. Restoration of the calcium is followed by a rise of the coagulation point to the normal level. Addition of excess of soluble calcium salt elevates the point somewhat. Decalcification changes the fibrinogen in another way; it is precipitated by an unusually low percentage of sodium chloride, beginning with 5 per cent. No similar lowering of coagulation point was seen in solutions of muscle proteids, egg albumin, and serum proteids. W. D. H.

Anti-rennin in the Serum of Fishes and Invertebrates. J. SELLIER (*Compt. rend.*, 1906, 142, 409—410).—The blood-serum of several groups of lower animals, like that of the higher, have the power of preventing the coagulation of milk by rennet. The power is destroyed at 62°. The activity varies in different animals, and quantitative details are given for various fishes, molluscs, and crustaceans.

W. D. H.

Variations in Toxicity of the Intestinal Contents. Modifications of the Blood. ALBERT CHARRIN and LE PLAY (*Compt. rend.*, 1906, 142, 524—527).—The toxicity of saline extracts of the intestinal contents varies in different parts of the canal, and usually the contents of the stomach are less toxic than those of the duodenum. The toxicity is rather increased by ligation of the bile duct, and, in the absence of bile, micro-organisms are more active in the intestine. The action of the poison is to modify the respiratory rhythm, to produce sensory and motor disorders, and to lower blood-pressure. Coagulation of the blood is delayed somewhat, the blood corpuscles become deformed, and hæmoglobin is diminished. Attempts to obtain an antitoxin failed.

W. D. H.

Rôle of the Pancreas in the Digestion and Absorption of Carbohydrates. UGO LOMBEROSO (*Beitr. chem. Physiol. Path.*, 1906, 8, 51—58).—After ligation of the pancreatic ducts there is no increase in the amylolytic action of other juices in the intestine; the normal or nearly normal absorption of carbohydrates which continues must be explained otherwise, and the pancreas must exert some action leading to carbohydrate absorption other than the mere secretion of an amylolytic ferment. Glycæmia and glycosuria do not occur on ligation of the ducts, as they do when the pancreas is extirpated.

W. D. H.

Glycolysis. IV. OTTO COHNHEIM (*Zeit. physiol. Chem.*, 1906, 47, 253—285. Compare Abstr., 1905, ii, 839).—Muscle extracts produce more or less diminution of the reducing power of dextrose solutions. The addition of pancreas increases the glycolysis in a marked degree. The glycolysis is not due to impurities or to bacteria, but is a function of one of the substances contained in the muscle itself. This is the main conclusion drawn from a new series of experiments designed to establish the author's opinions expressed previously on the subject.

W. D. H.

Chemical Dynamics of Animal Nutrition. SAMUEL B. SCHRYVER (*Bio-chem. J.*, 1906, 1, 123—166).—This paper contains a discussion of current theories of metabolism, especially in relation to proteids, and an account of researches on the same subject approached mainly by experiments on autolysis. Controversy has arisen as to whether the products of tryptic proteolysis are discoverable in the blood. To settle this difficult problem, a trustworthy method of estimating coagulable protein is essential; the difference between the nitrogen of coagulable protein and the total nitrogen is termed "residual nitrogen." The method employed consists in mixing the fluid

or tissue with anhydrous sodium sulphate; the water is thus abstracted and the mixture can then be dried at 38° . This can be kept without alteration for a considerable time; the total nitrogen is estimated by Kjeldahl's method. A sample is then coagulated by boiling with absolute alcohol, and, after washing, the nitrogen in the coagulum is estimated in the same way. In blood, liver, and mucous membrane of the small intestine, the residual nitrogen was never greater in fed than in fasting animals; in the case of blood, the numbers are practically identical. Furthermore, no substance giving the biuret reaction was ever detected in the filtrate from the coagulum. In the liver, the residual nitrogen is larger in fasting animals; this is due to autolysis already taking place at the time of death; substances giving the biuret reaction are also absent. In the intestinal mucous membrane, the residual nitrogen is constant for the same species of animal and is not influenced by the state of nutrition. It is higher in carnivora than in herbivora, and higher than in any other tissue; this tissue also is peculiar in the fact that disintegration commences immediately it is incubated with water, and some figures quoted indicate that some of the substances represented by the residual nitrogen are in some form of chemical combination in the protoplasm.

From these facts, the following explanation of the mechanism is advanced: the passage of the tryptic products through the mucous membrane is analogous to a continuous chemical process: the bioplasm acts as an enzyme or collection of enzymes to specific points of which side-chains are attached; it remains always saturated with side-chains, even in the absence of digested food; in the latter case, the autolytic enzyme steps in. This acts (in the liver) more rapidly in the fasting state, is inhibited by ammonia and other alkalis, and is accelerated by acids, especially lactic acid. Ammonia is formed in the alimentary tract, and there is more ammonia in the portal vein than in any other part of the body, and more is obtainable from the liver of a fed than of a fasting animal. The conclusion is therefore drawn that in order to maintain nitrogenous equilibrium, nitrogenous food must be ingested in such amounts and in such a form that the ammonia produced therefrom in the digestive tract is sufficient to maintain the intracellular alkalinity of the liver and probably other tissues. During fasting, non-nitrogenous acidic substances are produced which exceed the amount of ammonia available, and the autolytic enzyme then comes into play.

The animal derives most of its energy from carbohydrates, and rapidly eliminates nitrogen from proteids; nevertheless, the latter are essential not only to satisfy the needs of endogenous metabolism (Folin), but also to maintain the proper alkalinity of the tissues; if this fails, nitrogenous equilibrium ceases to be maintained.

Speck has drawn attention to four cases in which tissue degradation sets in, namely, lack of oxygen, phosphorus poisoning, withdrawal of water, and fever. The bearing of the conclusions on these abnormal conditions is discussed.

W. D. H.

The Fate of Certain Amino-acids and Peptides in the Organism of the Dog. EMIL ABDERHALDEN and YUTAKA TERUUCHI (*Zeit. physiol. Chem.*, 1906, 47, 159—172).—The nitrogen contained in

glycine and alanine, in glycyl-glycine and diglycyl-glycine, and in glycine anhydride and alanine anhydride is utilisable by the organism of the dog, participating in metabolism, and being excreted mainly as urea.

W. D. H.

The Fate of Choline in the Animal Body. HEINRICH VON HOESSLIN (*Beitr. chem. Physiol. Path.*, 1906, 8, 27—37).—Lecithin is a fairly abundant constituent of food, and, although some is absorbed unchanged (Slowtsoff), most observers agree that the major part is broken up in the intestine into choline, fatty acid, and glycerophosphoric acid. Hasebroek considers that the choline is entirely decomposed into methane and carbon dioxide by the intestinal bacteria, but its ready solubility and diffusibility show that it can remain long in the intestine; moreover, after feeding on choline, Nesbitt (*J. Exp. Med.*, 4, 1) found it in the chyle. After subcutaneous injection in doses of one gram, Gumprecht found it in the urine, but this does not occur with smaller doses (Halliburton and Mott, Donath), and it is absent from normal urine. In the present experiments, it was administered to rabbits both by the mouth and subcutaneously in doses of from 0.5 to 2 grams of the hydrobromide. It was never found in the urine, and so must be changed after absorption. The excretion of formic acid in the urine shows great variations in health; in spite of this inexplicable inconstancy, it can nevertheless be shown that there is usually a marked increase in it after the administration of choline, but the increase only accounts for a small portion of the base given; the remainder is probably fully oxidised to form carbon dioxide and water. Glyoxylic acid was only once detected in the urine, and there is no increase in the creatinine discharged. The increase of formic acid in the urine in cases of fever and leucæmia may be due to the break down of the lecithin of cells.

W. D. H.

Ferments of the Placenta. ALBERT CHARRIN and GOUPIL (*Compt. rend.*, 1906, 142, 595—597).—Former experiments have shown that the placenta retains various substances, particularly dextrose; the present research was undertaken to determine whether this organ contains ferments capable of altering or destroying the retained material. Placental extracts were found to contain an amylolytic ferment, an oxydase, and a glycolytic agent. A proteolytic ferment also present is attributed to admixture with blood. Ferments acting on fats or on lactose were not discovered.

W. D. H.

Erepsin. OTTO COHNHEIM (*Zeit. physiol. Chem.*, 1906, 47, 286).—Erepsin is present in the intestine of dogs from which the pancreas has been extirpated, and is as active as in normal animals.

W. D. H.

Dextrose in Hydrocele Fluid. GUSTAVE PATEIN (*J. Pharm. Chim.*, 1906, [vi], 23, 239—241).—Four specimens of hydrocele fluid were examined, three of which were found to contain dextrose to the extent of from 0.60 to 1.50 grams per litre. The dextrose present in these specimens did not diminish when they were kept for twenty-four hours,

whence it appears that the absence of this sugar in the fourth specimen was not the result of any action occurring after the fluid was collected.

T. A. H.

Is the Passage of Food-fat into the Milk proved by Winternitz's Experiments with Iodised Fats? S. GOGITIDSE (*Zeit. Biol.*, 1906, 47, 475—486).—Polemical, mainly against Caspari.

W. D. H.

Milk Treated with Hydrogen Peroxide. PAUL ADAM (*J. Pharm. Chim.*, 1906, 23, 273—277).—Fresh, unboiled milk gives, in the presence of hydrogen peroxide, the well-known reactions with guaiacum and *p*-phenylenediamine and decolorises Schardinger's reagent (*Abstr.*, 1903, ii, 190). The same milk when decomposed does not give the first two reactions, but still decolorises Schardinger's reagent. Unboiled milk containing hydrogen peroxide reacts with guaiacum and with *p*-phenylenediamine, but not with Schardinger's test, whilst if kept until the hydrogen peroxide has disappeared it gives the same reactions as fresh milk with guaiacum and *p*-phenylenediamine, but does not decolorise Schardinger's reagent. The author concludes that the reducing ferment in milk is at once destroyed by hydrogen peroxide, but that the oxidising ferment (not to be confused with the oxydase) remains unaffected for a considerable time.

W. P. S.

The Influence of Intake of Water on the Excretion of Nitrogen and Chlorides. ERNST HEILNER (*Zeit. Biol.*, 1906, 47, 538—561).—In inanition, in contrast with what occurs in a well-fed condition, the administration of water produces an increase in nitrogenous excretion. This is due to breaking down of the nitrogenous body-substance, and not merely to a washing out of nitrogenous katabolites from the tissues. The chlorides excreted are increased similarly, and here again it is held that this is not merely a washing out. There is no direct and simple relationship between the nitrogen and chlorides of the urine in fasting animals. The increased output of chlorides due to intake of water is not so immediate as that of nitrogen, and extends over several days.

W. D. H.

Excretion of Creatine and Creatinine in Man. KJ. OTTO AF KLERCKER (*Beitr. chem. Physiol. Path.*, 1906, 8, 59—61).—On food free from creatine, however much the proteid intake may vary, the excretion of creatinine remains constant, as Folin states. If food containing creatine is taken, or creatine added to the diet in known amount, the substances which pass into the urine are creatine and creatinine; but of the exogenous creatine given little or none is converted into creatinine; if creatinine is added to the food, some passes as such into the urine; if both are added, more creatinine is recovered from the urine than creatine. But the total of either never amounts to the total administered. In one case, 89 per cent. of the creatine given was again found in the urine, but the more usual number is 20 to 30 per cent. These experiments on the author's own person are preliminary to an investigation of the subject in disease, a subject rendered easy by Folin's colorimetric method.

W. D. H.

Clinical Estimation of the Alkalinity of the Blood. MERCIER GAMBLE (*J. Path. Bact.*, 1906, 11, 124—166).—Titration with an organic acid is unnecessary; a dilute inorganic acid does not precipitate proteids in sufficient amount to influence the results. Lacmoid is the best indicator. A dilute albuminous solution and an equal volume of dilute alkaline solution have a greater acid-combining power when titrated together than when titrated separately.

The alkalinity of the blood in the healthy adult is equivalent to about 300 mg. of sodium hydroxide per 100 c.c. The variations in health are slight; a rise occurs after the mid-day meal (alkaline tide). In anæmia, the alkalinity is lessened. The lowest results were obtained in chlorosis, leucæmia, and diabetes, with some evidence of acid intoxication.
W. D. H.

The Blood-glands as Pathogenic Factors in the Production of Diabetes and Obesity. ARNOLD LORAND (*Trans. Path. Soc.*, 1906, 57, 1—20).—A discussion, mainly theoretical, of various views held on the above subject. The glands in question are regarded as factors in the diseases mentioned.
W. D. H.

Paroxysmal Hæmoglobinuria. JOHN EASON (*J. Path. Bact.*, 1906, 11, 167—202, 203—208).—A discussion of the etiology and pathology of paroxysmal hæmoglobinuria, written mainly on immunity lines, but no conclusions, with any certainty, are drawn. The excretion of nitrogen is diminished during the paroxysms, but the proportion of urea is increased. A serum containing an antitoxin was obtained from guinea pigs treated with injections of serum from patients with the disease. So far, experiments with the antitoxic serum have only been made *in vitro*.
W. D. H.

Opsonic Content of the Serum in the Course of Acute Pneumonia. G. G. MACDONALD (*Trans. Path. Soc.*, 1906, 57, 45—52).—In the majority of patients suffering from staphylococcal or tubercular infection, the opsonic index is lower than normal. The same is true of pneumococcal infections and in the precritical period of acute pneumonia. If the index does not rise, the prognosis is serious. The high index in cases of closed empyema is due to immunisation from products absorbed from the pleural cavity. No constant relation between the amount of opsonin in the serum and the degree of leucocytosis could be discovered.
W. D. H.

Agglutinin Test in Tuberculosis. JOSEPH T. WIGHAM (*J. Hygiene*, 1906, 6, 212—214).—During the progress of a tuberculous infection in monkeys, no agglutinative titrate of any diagnostic value could be obtained in either early or late stages of the disease. Whether the agglutinative reaction is of any value in the diagnosis of human tuberculosis has been differently answered by different observers.
W. D. H.

Quantitative Action of Poisons. THOMAS BOKORNY (*Pflüger's Archiv*, 1906, 111, 341—375. Compare following abstract).—A

further contribution to the action of many poisons, organic and inorganic, on the cell protoplasm mainly of algæ. W. D. H.

The Toxicity of Aniline Dyes. THOMAS BOKORNY (*Chem. Zeit.*, 1906, 30, 217—219).—Various aniline dyes act injuriously on micro-organisms, and quite dilute solutions are fatal. The dye unites with the protoplasm, although whether real chemical combination occurs is not decided. W. D. H.

Toxicity of Bile. II. SAMUEL J. MELTZER and WILLIAM SALANT (*J. Exper. Med., New York*, 1906, 8, 1—40. Compare Abstr., 1905, ii, 836).—Bile causes hyperæsthesia and tetanic attacks when injected into frogs, but stagnant bile from the gall-bladder produces coma and paralysis. The depressive element is by far the stronger, and when the exciting element is present also, the effect is the result of the algebraic sum of the two. Nephrectomy increases the exciting element, and can be imitated by subcutaneous injections of strychnine. By injecting a toxic dose of strychnine into a frog soon after it has received a depressing dose of bile, an eclamptic state can sometimes be produced. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Importance of Strictly Anaërobic Putrefactive Bacili for the Ripening of Cheese. ANTONIO RODELLA (*Centr. Bakt. Par.*, 1906, ii, 16, 52—66).—A reply to von Freudenreich (*Die Bakteriologie in der Milchwirtschaft, Jena*, 1906) with regard to the production of fatty acids by anaërobic bacilli. Results obtained with those of the hexoic, valeric, and butyric acid groups are given.

N. H. J. M.

Toxin of the *Bacillus enteriditis* of Gärtner. E. PROVAN CATHCART (*J. Hygiene*, 1906, 6, 112—122).—Poisoning by meat infected with this bacillus is especially to be feared because there is but little putrefactive smell, and the toxin, like that of the paratyphoid bacillus, but unlike that of colon bacilli, will stand a temperature of 100° for thirty minutes without change. In the present experiments on mice, which are very susceptible to the toxin, the relation between virulence of the bacilli and toxicity of the product does not appear to be very definite. The toxin is of the endotoxin type, and the most poisonous preparations were obtained by autolysis of the bacilli in the presence of distilled water or normal saline solution for about eight or nine days. Too long autolysis yields an innocuous product. The autolysis is accelerated by the presence of toluene, but chloroform kills the culture and leads to loss of toxicity. W. D. H.

Streptococci and Leucocytes in Milk. WILLIAM G. SAVAGE (*J. Hygiene*, 1906, 6, 123—138).—Leucocytes are always present in ordinary milk obtained in the usual way from cows apparently free from disease. In cows with inflamed udders, the number is greater. Streptococci are always present also, but are increased by inflammatory conditions. A method of centrifugalisation and microscopic examination is described for ascertaining the number of these two formed elements. Such preliminary experiments are necessary with a view to obtaining a standard of what is and what is not healthy milk, and where the number of leucocytes amounts to pus-admixture. The presence of *Bacillus coli* is a definite indication of contamination after milking, during milk collection or storage. W. D. H.

Rôle of Organic Matter in Nitrification. ACHILLE MÜNTZ and E. LAINÉ (*Compt. rend.*, 1906, 142, 430—435).—Humus, in whatever quantity, is favourable to nitrification, probably owing to the multiplication of nitrifying organisms. There is no reason to fear any injurious action in the employment of substances rich in humus in nitrate beds.

Comparing the effects of different soils on the same amount of ammonium sulphate, it was found that the rich soils nitrified much more quickly than sandy or clay soils. At the end of seven days, the richest soil, containing 17.6 per cent. of carbon, nitrified 0.209 gram of nitrogen per kilogram, whilst a soil containing 1.5 per cent. of carbon nitrified only 0.02 gram. At the end of thirty-two days, however, after further additions of ammonium sulphate, the differences in the amounts of nitric nitrogen were much less, so that the presence of much organic matter, although desirable, is not essential.

N. H. J. M.

Fruit Wine Yeasts. A. OSTERWALDER (*Centr. Bakt. Par.*, 1906, ii, 16, 35—52).—The chief yeasts of fruit wines show marked morphological differences, but do not differ much physiologically. Detailed analyses of the wines would probably show typical differences.

N. H. J. M.

Decomposition of Vegetable Foods [by Micro-organisms] in Absence of Air. JOSEF KÖNIG, ALB. SPIECKERMANN, and H. KUTTENKEULER (*Zeit. Nahr. Genussm.*, 1906, 11, 177—205).—The nature of the decomposition of foods is the same in absence as in presence of oxygen, but there is considerable difference in the quantity of the products. The loss of dry matter is only slight in absence of air. In both cases the chief loss is in the non-nitrogenous extract substances. The amount of pentosans is much reduced in presence of air, whilst the crude fibre and ether extract remain about the same. Loss of total nitrogen is only appreciable in presence of air; the proteids decompose only slightly in absence of air, whilst in presence of air they are mostly decomposed with production of simpler compounds, including ammonia. Foods which have been kept without access of air become strongly acid, without, however, changing in appearance. In presence of air, foods become strongly alkaline.

Decayed cotton-seed meal and cocoanut meal may be given for a long time to goats and sheep without injury to health.

N. H. J. M.

Mechanism of Carbon Assimilation in Green Plants. FRANCIS L. USHER and J. H. PRIESTLEY (*Proc. Roy. Soc.*, 1906, B, 77, 369—376. Compare Bach, Abstr., 1893, ii, 483 ; H. Euler, Abstr., 1904, ii, 761).—Some years ago, Bach claimed to have obtained formaldehyde and uranium peroxide by the action of carbon dioxide on uranium acetate in sunlight ; in this process, the uranium salt is supposed to play the part of a chemical and optical sensitiser. The authors have confirmed Bach's results, but find that even after three weeks' exposure in bright weather the amount of decomposition is very small. Experiments were also made with higher concentrations of carbon dioxide by exposing sealed tubes containing the liquefied gas and uranium acetate solution to sunlight ; in this case, uranium peroxide and formic acid were rapidly produced, but not formaldehyde. Since, for obvious reasons, objections might be raised to the use of uranium acetate, the experiments were repeated with 2 per cent. solutions of the sulphate, and in this case also the peroxide and formic acid, but not formaldehyde, were obtained.

If a corresponding process takes place in the plant, leading to the production of formaldehyde and hydrogen peroxide, it is clear that these substances undergo rapid change, so that it is useless to search for them in the assimilating leaf under ordinary conditions. The authors adduce evidence to show that the hydrogen peroxide is rapidly split up by a catalysing enzyme which they have succeeded in isolating from *Elodea* leaves ; they further examined leaves of numerous typical natural orders and found all to have the property of splitting up the peroxide, so that the enzyme appears to be of general occurrence. Very dilute solutions of formic aldehyde inhibit the catalysing action of this substance. That it is located at the seat of the photosynthetic process was proved by microscopic examination of *Elodea* leaves in very dilute hydrogen peroxide ; bubbles of oxygen were given off from the chloroplasts only.

With the object of rendering possible the detection of formaldehyde by destroying the agent which so rapidly effects its condensation under ordinary conditions, green sprigs of *Elodea* were immersed in boiling water for thirty seconds to kill the protoplasm and destroy the enzymes, and were then placed in water saturated with carbon dioxide and exposed to sunlight. The green colour disappeared in a few hours and the bleached twigs gave the aldehyde reaction with Schiff's reagent. This experiment was repeated on a larger scale with the green parts of two other plants ; the bleached leaves were subjected to steam distillation and the presence of formaldehyde in the filtrate conclusively proved by the methylenedianiline and tetrabromohexamethylenetetramine tests. In order to determine whether the condensation of formaldehyde is effected by an enzyme or by the living protoplasm, the latter was killed by exposure to chloroform vapour ; in the leaves so treated formaldehyde could readily be detected after exposure to sunlight under the usual conditions—a result which shows that the living protoplasm is the condensing agent.

The authors account for the above observations as follows: in the experiment in which both protoplasm and enzymes were initially destroyed, the accumulating peroxide bleaches the chlorophyll and the process is thus brought to a standstill; by this time an equivalent amount of formaldehyde has been produced and can readily be detected. When the protoplasm is killed, but not the enzymes, the formaldehyde poisons the latter with the result that the accumulating hydrogen peroxide bleaches the chlorophyll and prevents further action. G. S.

Consumption of Nutrients by Parent Beets and Seedlings. KARL ANDRĚK, VLADIMÍR STANĚK, and J. URBAN (*Zeit. Zuckerind. Böhm.*, 1906, 30, 165—173).—The supply of nutritive substances in sugar-beet roots at the end of the first year of growth amounts to only 8—10 per cent. of the amount required for the second year. The amount consumed by seed roots, whether seedlings or parent roots, will vary according to the soil and the amount of seed produced. Small seedlings require less nutritive matter than large ones for producing the same amount of seed. N. H. J. M.

Root-sap Acidity. WALTER F. SUTHERST (*Chem. News*, 1906, 93, 131—132).—The yield of wheat grown in soil containing chalk diminished as the percentage of chalk increased. The length of the roots and the relation of roots to shoots increased, the acidity of the root-sap diminished slightly, and the percentage of ash in the dry matter diminished considerably with increased amounts of chalk in the soil. N. H. J. M.

Apple Marc. WILLARD D. BIGELOW and HERBERT C. GORE (*J. Amer. Chem. Soc.*, 1906, 28, 200—207).—When apple marc is fractionally extracted with boiling water, it yields products amounting to 40 per cent. of its weight, including a single carbohydrate complex, a galacto-araban, which is gradually rendered soluble during the boiling and appears in all the fractions. The various fractions were analysed separately. On evaporating the aqueous extract, a residue is obtained which forms nearly transparent leaflets, has a slightly acid taste, dissolves in water to form a viscid, cloudy liquid, and is precipitated by alcohol as a jelly. From the analysis of the extracts and the residue, the dry apple marc was found to have the following composition: pentosans, 24.51 per cent.; extracted pentosans (in hot water extracts), 15.50; extracted galactans (in hot water extracts), 12.96; cellulose, 40.19 (containing 5.51 per cent. of pentosans); crude fibre, 30.90 (containing 2.92 per cent. of pentosans); reducing sugar, 1.67; proteids, 3.43; ethereal extract, 0.74; and ash, 0.95 per cent.

If the must of apples is treated with several times its volume of alcohol, an opaque, yellowish-brown, gelatinous precipitate is produced in which the ratio of galactans to pentosans is much higher than in the aqueous extract of apple marc.

By adding alcohol to "second pressing" cider, a product is obtained which has an acid taste, forms opalescent solutions, and in which the ratio of galactans to pentosans is 1.4, whilst the ratios in the cases of the extract of apple marc and the precipitate from the must are about 0.8 and 1.8 respectively. E. G.

Cyanogenetic Beans of *Phaseolus lunatus*. L. GUIGNARD (*Compt. rend.*, 1906, 142, 545—553. Compare Dunstan and Henry, *Abstr.*, 1904, ii, 71; *Bull. Imp. Inst.*, 1905, 3, 373; Robertson and Wynne, this vol., ii, 112).—The amount of hydrocyanic acid obtainable from the ground beans was determined by macerating in water at 30° for twenty-four hours, distilling, and titrating the distillate with silver nitrate solution. Java beans yielded from 0·052 to 0·102 per cent., Burmah beans from 0·006 to 0·015 per cent., Madagascar beans from 0·008 to 0·027 per cent., and three varieties, cultivated in Provence, from “traces” to 0·008 per cent. These results differ from those of previous investigators in that white cultivated beans of *P. lunatus* are now shown to yield minute quantities [“traces” to 0·008 per cent.] of hydrocyanic acid, and that the white beans, which occur rather sparsely in Java beans, yield as much hydrocyanic acid as the coloured varieties. Attention is directed to the fact that the beans remain poisonous even after boiling, since this process merely destroys the enzyme and not the cyanogenetic glucoside. T. A. H.

Fruits of *Sapindus Rarak*. O. MAY (*Arch. Pharm.*, 1906, 244, 25—35).—A morphological description of the seeds is first given.

The saponin was isolated from the powdered husks by neutralising the free phosphoric acid they contain with magnesium oxide, extracting with hot 90 per cent. alcohol, removing resinous impurities from the alcoholic extract by shaking it with light petroleum, precipitating the saponin with ether, dissolving it in alcohol, boiling the solution for a considerable time with neutral lead hydroxide, and precipitating fractionally with ether. Methyl alcohol dissolves 4·6 per cent. of it; ethyl alcohol, 1·75 (96 per cent. alcohol, 2·85); amyl alcohol of sp. gr. 0·82, 0·2; acetone of sp. gr. 0·798, 0·17 per cent. The limit of its hæmolytic action, as measured by the strength of the solution which will just completely clear a 1 per cent. solution of blood, is 1:15,000 for dog's blood, 1:12,000 for rabbit's blood. It is amorphous, and has the formula $C_{24}H_{42}O_{15}$ (molecular weight determined). It forms an amorphous *acetyl* derivative, $C_{24}H_{23}O_{15}Ac_9$. When it is heated with 5 per cent. hydrochloric or sulphuric acid, one molecule of it yields one molecule each of *sapogenin*, $C_{12}H_{18}O_3$ (molecular weight determined), pentose, and hexose; the *osazones* of the latter two, separated by fractional crystallisation, melted at 160° and 196°.

The husks yielded 13·5 per cent. of saponin and 2·3 per cent. of ash containing 22·2 per cent. of phosphoric acid.

The embryo, freed from husk, yielded 26·2 per cent. of a yellow, non-drying oil of sp. gr. 0·911 at 15°, acid number 5·3, saponification number 170·2, iodine number 65·1, Reichert-Meissl number 0·7, and Hehner number 80·1. The fatty acids insoluble in water which were obtained from the oil consisted of oleic acid 80, palmitic acid 16, and stearic acid 4 per cent. C. F. B.

Buckwheat. EMIL HASELHOFF (*Landw. Versuchs-Stat.*, 1906, 63, 375—406).—Statistics relating to the production of buckwheat in different countries, its cultivation, chemical composition, and food value. N. H. J. M.

Amount of Combined Nitrogen in Rain and Dew. JOHN W. LEATHER (*Ann. Rep. Imp. Dept. Agr.* for the year 1904-5, 55-57).—The rain-water collected at Dehra Dun and Cawnpore during twelve months contained the following amounts of nitrogen as ammonia and nitrates. The date is not given.

	Rainfall, inches.	Nitrogen per million		Nitrogen per acre (lb.)		
		as NH_3 .	as N_2O_5 .	as NH_3 .	as N_2O_5 .	Total.
Dehra Dun	87.45	0.110	0.070	2.178	1.391	3.569
Cawnpore	49.36	0.222	0.069	2.482	0.768	3.250

The percentages of ammonia nitrogen and nitric nitrogen in the total nitrogen were 61.0 and 39.0 in the rain collected at Dehra Dun, and 76.4 and 23.6 at Cawnpore. In dew, the nitric nitrogen was generally equal to, and sometimes exceeded, the nitrogen as ammonia.

N. H. J. M.

[Amount of Nitrogen as Ammonia and Nitrates in Rain-water collected at Pretoria.] HERBERT INGLE (*Transvaal Agric. J.*, 1905, 4, 104-105).—Determinations of ammonia and nitrates and nitrites were made in weekly samples of the rain-water collected at Pretoria from July 1, 1904, to June 30, 1905. The results for the whole year are as follows:

Rainfall, inches.	Nitrogen per million		Nitrogen per acre (lb.)			Percentage of total N.	
	as NH_3 .	as N_2O_5 .	as NH_3 .	as N_2O_5 .	Total.	as NH_3 .	as N_2O_5 .
24.31	1.194	0.196	6.587	1.083	7.670	85.9	14.1

The nitrogen as ammonia varied from 0.32 (week ending March 18) to 45.0 (week ending Aug. 27) per million, the rainfall being 70.36 mm. and 1.06 mm. respectively. The nitrogen as nitrates varied from 0.03 to 3.75 per million (rainfall 10.08 and 0.38 mm.).

Nearly the whole of the nitrogen in the rain is brought down during the growing season.

N. H. J. M.

Use of Metallic Copper for the Purification of Drinking Water. HENRY KRAEMER (*Amer. J. Pharm.*, 1906, 78, 140-144).—Further experiments prove that *Bacillus coli* and *B. typhosus* are completely destroyed by placing clean copper foil in the water containing them (compare Abstr., 1905, ii, 108). From personal experience, the author concludes that water thus treated has no toxic effects on man. There being a number of factors which tend to eliminate the copper in solution, it is hardly likely that water from a reservoir would contain any copper by the time it reached the consumer, provided that the treatment at the reservoir were in competent hands. W. P. S.

Copper Salts in Irrigating Waters. W. W. SKINNER (*J. Amer. Chem. Soc.*, 1906, 28, 361-368).—A study has been made of the effect produced on vegetation by copper salts, which are frequently carried in the waste products from the mining and working of copper ores into water supplies used for irrigation. It has been found that copper is injurious to plants even when the soil contains comparatively

large quantities of bicarbonate of calcium or magnesium. When a dilute solution of copper sulphate is added gradually to a solution containing 1.1075 grams of calcium hydrogen carbonate per litre and the solution is left for forty-eight hours, the clear liquid contains 0.2071 gram of copper per litre. A saturated solution of sodium hydrogen carbonate is capable of dissolving 953 parts of copper per million. A solution of sodium carbonate equivalent to a soil containing 0.05 per cent. of sodium carbonate is capable of holding 1.70 grams, and a solution equivalent to a soil containing 0.025 per cent. of sodium carbonate is capable of holding 0.40 gram of copper per million. The injurious effect of soluble copper salts on plants even when the soil contains large amounts of carbonates or bicarbonates is thus accounted for.

E. G.

Some New Properties of Soils. JOSEF KÖNIG, J. HASENBÄUMER, and C. COPPENRATH (*Landw. Versuchs-Stat.*, 1906, **63**, 471—478).—With the view of obtaining a method for determining the available constituents of soils, attempts were made (*ibid.*, 1905, **61**, 371) to destroy the colloidal condition of the soil by heating at about 200°. Better results have now been obtained by heating the soil (250 grams) in a linen bag suspended in a copper vessel containing 3 to 4 litres of water for three hours under a pressure of 4 atmospheres. The solution is then evaporated down, filtered, and evaporated to dryness and its different constituents determined. Analyses of six soils by this method are given. It remains to be determined at what pressure the greatest amounts of mineral matters are dissolved and their relation to the amounts utilised by plants.

The power which soils have of liberating oxygen from hydrogen peroxide is greatly reduced by heating in steam under three atmospheres' pressure; treatment with mercuric chloride, chloroform, and iodine had the same effect; whilst after treatment with hydrogen cyanide or boiling hydrochloric acid the soil only liberated traces of oxygen if any. Sea sand acted very slightly, and kaolin and albite only liberated traces of oxygen. The amounts of oxygen liberated by different soils are proportional to the intensity of the colour they produce with *p*-phenylenediamine, so that the properties referred to must be mainly due to catalases, and in a less degree to inorganic colloids.

A method is described for the preparation of membranes for experiments on the osmotic pressure of soils.

N. H. J. M.

Loss of Nitrogen in Soil Manured with Sodium Nitrate. JULIUS STOKLASA, JOHANN JELÍNEK, and ADOLF ERNEST (*Zeit. Zucker-ind. Böhm.*, 1906, **30**, 223—233).—The results of experiments with Bohemian sugar-beet soils showed that the organic matter present is not suitable as a source of carbon for denitrifying microbes, and that nitrates are not reduced to nitrogen to any appreciable extent.

Loss of nitrogen cannot occur when soils are well aerated by mechanical operations; reduction of nitrate to nitrite may, however, occur.

N. H. J. M.

Spontaneous Formation of Dicyanodiamide in Manures containing Calcium Cyanamide. RENATO PEROTTI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 48—53. Compare Abstr., 1905, ii, 870).—When manures containing calcium cyanamide are kept, the amount of the latter present gradually diminishes to nearly zero, the nitrogen-content at the same time undergoing only a slight decrease. The author shows that this is due to the spontaneous change of the calcium cyanamide into dicyanodiamide. T. H. P.

Action of Calcium and Magnesium in Burnt Lime, Marl, and Limestone Meal on the Assimilation of Mineral Substances by Different Crops. RICHARD ULBRICHT (*Landw. Versuchs-Stat.*, 1906, 63, 321—374).—An account of experiments made in 1896 to 1903 with various plants grown in cylinders.

Application of lime resulted in a slightly diminished assimilation of nitrogen and phosphoric acid in the case of lupins, vetches, and serradella, whilst the potassium was increased in lupins and serradella, but not in vetches. The magnesia in all three plants was considerably increased by manuring with calcium and magnesium carbonates, and was distinctly increased even by burnt Carrara marble, which contains only small amounts of magnesium. N. H. J. M.

Analytical Chemistry.

Modification of the Orsat Apparatus. LOUIS DE SAINT MARTIN (*Ann. Chim. anal.*, 1906, 11, 96—98).—The apparatus is connected with a manometer, thus enabling the operator to read off the volume of the gas before and after treatment with absorbents at the ordinary pressure. L. DE K.

New Apparatus. [Potash Bulbs. Porcelain-lined Bomb. Electrolytic Apparatus.] SALOMON F. ACREE (*Amer. Chem. J.*, 1906, 35, 309—316).—A new form of alkali apparatus is described, consisting of a cylindrical vessel containing two large glass bulbs through which the gas circulates and then passes away through a small calcium chloride tube. Both the bulbs and the outer vessel are filled with glass wool which is moistened with potassium hydroxide solution, and thus presents a large absorptive surface. With this apparatus, combustions can be conducted very rapidly without risk of any of the carbon dioxide escaping absorption.

A porcelain-lined bomb is described which is very useful for storing small quantities of gases, such as sulphur dioxide or ammonia, which are liquid only under pressure or at low temperatures, and is also serviceable in place of sealed tubes.

An apparatus has been devised for effecting rapid precipitation in

electrolytic analysis. It consists essentially of a beaker in which are suspended a platinum gauze electrode and a rotating electrode of heavy platinum foil. The rotating electrode forces all the solution to be electrolysed into contact with the gauze as often as desired, and thus ensures the rapid precipitation of the metal.

All these pieces of apparatus are fully described with the aid of diagrams. E. G.

Percolator for Use in Assaying Drugs. FRANK R. ELDRÉD (*J. Amer. Chem. Soc.*, 1906, 28, 187—188).—A cylindrical form of separating funnel about 30 cm. in length and of 100 c.c. capacity. The top is funnel-shaped and fitted with a stopper. After inserting the usual plug of cotton, the substance and solvent are introduced, and the whole is well shaken. During the maceration the stopper is kept in place by a spring clip. When starting the percolation, the stopper is washed with the solvent, and then placed in a slightly inclined position so as to prevent undue evaporation of the solvent.

L. DE K.

Convenient Preparation of Chloric Acid and its Application in Analysis, especially in the Estimation of Tin in Bronze and Brass. V. BERNARD (*Ann. Chim. anal.*, 1906, 11, 81).—Eight hundred grams of pure barium chlorate are dissolved in 1700 c.c. of hot water. When cold, 243 grams of sulphuric acid, previously diluted with water to about 2000 c.c., are slowly added, and the clear liquid is afterwards poured off from the barium sulphate deposited.

In combination with hydrochloric acid, this reagent is preferable to potassium chlorate in the oxidation of numerous substances. It is particularly recommended for dissolving tin sulphide when the metal has to be determined finally by electrolysis.

L. DE K.

Estimation of Sulphur in Pyrites. FRITZ RASCHIG (*Zeit. angew. Chem.*, 1906, 19, 331—334).—The author recommends his "benzidine process" (Abstr., 1903, ii, 572, 691) for the estimation of sulphur in iron pyrites.

0.8 gram of the finely-powdered sample is boiled with 5 c.c. of fuming nitric acid until perfectly decomposed and then diluted with water to 100 c.c. Twenty c.c. of the solution are mixed with 10 c.c. of a 1 per cent. solution of hydroxylamine hydrochloride, and then with 500 c.c. of the benzidine reagent. After fifteen minutes, the benzidine sulphate is collected, washed, and titrated with *N*/10 sodium hydroxide as usual.

L. DE K.

Estimation of Sulphurous Acid in Flesh. CURT MENTZEL (*Zeit. Nahr. Genussm.*, 1906, 11, 320—324).—Nine samples of minced beef examined by the author yielded, when distilled with phosphoric acid in a current of carbon dioxide, from 0.0014 to 0.0021 per cent. of sulphur dioxide. The addition of 10 per cent. of onions increased the yield of sulphur dioxide by 0.0006 per cent., and minced onions themselves gave only 0.0058 per cent. of sulphur dioxide. The author concludes that samples giving more than 0.004 per cent. of sulphur

dioxide, or more than 0.005 per cent. in the cases where onions are present, should be considered as containing added sulphite.

W. P. S.

Estimation of [Combined] Sulphuric Acid in Drinking Water. FRITZ RASCHIG (*Zeit. angew. Chem.*, 1906, 19, 334).—0.5—5 litres of water are mixed with one-twentieth part of the author's benzidine reagent (*Abstr.*, 1903, ii, 691) and allowed to remain for fifteen minutes. Should the sample be ferruginous, 1—2 c.c. of hydroxylamine solution are added first. The precipitated benzidine sulphate is treated as directed previously. On account of the slight solubility of the compound, an allowance should be made of 1.5 mg. of sulphur trioxide per litre.

L. DE K.

Phosphorus and the Sulphides of Phosphorus. A. SIEMENS (*Chem. Zeit.*, 1906, 30, 263—264 and 271—272).—Attention is drawn to the fact that no satisfactory methods are known for detecting the presence of free yellow phosphorus in phosphorus preparations, more especially in those containing sulphur.

P. H.

Estimation of Minute Quantities of Arsenic [in Sulphuric Acid]. H. B. BISHOP (*J. Amer. Chem. Soc.*, 1906, 28, 178—185).—Two hundred and fifty c.c. of sulphuric acid are heated to the boiling point in a distilling flask, and a mixture of hydrochloric and sulphurous acids is introduced through a capillary tube at the rate of 50—75 c.c. per hour. The escaping vapours are condensed in water, the solution is oxidised with potassium chlorate, concentrated on the water-bath to 5—10 c.c., and then at once tested in a small Marsh apparatus.

The process may also be applied to foods, &c. Ten grams of the dried material are heated with 250 c.c. of pure sulphuric acid, and the resulting liquid is treated as above.

L. DE K.

Arsenic in "Pure Glycerins." J. GALIMARD and E. VERDIER (*J. Pharm. Chim.*, 1906, [vi], 23, 183—184).—"Pure glycerin" of commerce frequently contains an arsenical compound [glyceryl arsenite?], which cannot be detected by the application of the Marsh test to the crude material. In such a case a sample of the glycerol is diluted with twice its volume of distilled water, previously acidified with dilute [1 per cent.] sulphuric acid, and the mixture is boiled for six hours in a reflux apparatus. The liquid can then be used for the Marsh test.

T. A. H.

Simplified Method of Elementary Analysis for Technical Purposes. MAX DENNSTEDT (*Zeit. angew. Chem.*, 1906, 19, 517—520. Compare this vol., ii, 51).—The author has given up the use of platinised quartz as contact substance, replacing it either by a coil of platinum foil or wire, or still better by a strip of platinum foil, at one end of which other strips are fixed radially, so that it has a sort of star-shaped section, and will just pass into the combustion tube.

L. DE K.

Assay of [Potash] Saltpetre. R. BENSEMANN (*Zeit. angew. Chem.*, 1906, 19, 471—473).—The oxalic acid process for the assay of Chili-saltpetre (Abstr., 1905, ii, 481, 555) may also be used for the assay of ordinary saltpetre, but in this case it is necessary to use twice the amount of oxalic acid. It is, however, more convenient to convert the nitrate into chloride by repeated evaporation with hydrochloric acid and then to allow for pre-existing chlorine compounds. L. DE K.

Gravimetric Estimation of Calcium. OTTO BRUNCK (*Zeit. anal. Chem.*, 1906, 45, 77—87).—A criticism of the various methods for the estimation of calcium, namely, weighing as oxalate, carbonate, sulphate, or oxide. The weighing as oxalate or oxide is not to be recommended.

A new process is given. The ignited oxalate is treated with a slight excess of hydrofluoric acid, the excess is carefully evaporated, and the residue heated to redness for five minutes. It consists of calcium fluoride, which is a very fit form for weighing the metal, as it suffers no loss on prolonged heating and also is not at all hygroscopic.

L. DE K.

Co-operative Analysis of an Argillaceous Limestone. [WILLIAM F. HILLEBRAND, CHARLES B. DUDLEY, CLIFFORD RICHARDSON, and HENRY N. STOKES] (*J. Amer. Chem. Soc.*, 1906, 28, 223—239; also compare Abstr., 1905, ii, 197).—Result of analysis of a carefully prepared specimen of argillaceous limestone by thirty-five different analysts—instructors and students. The main constituents (silica, calcium, &c.) were on the whole reported very accurately, but such constituents as alumina, manganese, alkalis, and combined water were determined very unsatisfactorily as a rule.

L. DE K.

Schlagdenhaufen's Reaction [Detection of Magnesium]. LÉON GRIMBERT (*J. Pharm. Chim.*, 1906, [vi], 23, 237—239).—The solution of sodium hypoiodite employed by Schlagdenhaufen as a test for magnesium is unstable and not very sensitive. The author suggests instead the addition of a few c.c. of a 10 per cent. solution of potassium iodide to the liquid under examination, followed by one or two drops of sodium hypochlorite solution (Eau de Javal), when, if magnesium is present, a red coloration or a brownish-red precipitate is formed. This precipitate may be magnesium hypoiodite; when washed with water, it is converted into magnesium hydroxide. The reaction is less delicate than the precipitation of ammonium magnesium phosphate. Neither lithium nor the alkaline earth metals gives a similar reaction.

T. A. H.

Estimation of Cadmium. HENRI BAUBIGNY (*Compt. rend.*, 1906, 142, 577—580).—The methods suggested by Follenius (this Journal, 1875, 481, 780) for avoiding the error to which the estimation of cadmium as the sulphide is liable, through cadmium sulphide carrying down (1) a small amount of the original cadmium salt and (2) a small quantity of free sulphur, are discussed. It is pointed out that cadmium sulphide is not reduced by organic matter (for example, carbonised filter paper) until heated with it above 500°, and consequently when the precipi-

tated sulphide contains no volatile or readily decomposed cadmium salt, it may with advantage be converted into the sulphate by the usual process and weighed as such. The results of a series of determinations quoted in the original indicate that this method is trustworthy.

T. A. H.

Iodometric Estimation of Copper. PAUL GERLINGER (*Zeit. angew. Chem.*, 1906, 19, 520—522).—The well-known iodometric estimation of copper in acetic acid solution suffers from the defect that the end reaction is somewhat obscure. According to the author, this may be remedied by adding to the solution, which should not exceed 20 c.c., so much solid potassium iodide that the cuprous iodide is completely redissolved. The liquid is then titrated with thiosulphate as usual.

L. DE K.

Assay of Mercury Ores. GEORGE T. HOLLOWAY (*Analyst*, 1906, 31, 66—71).—The finely-powdered ore is mixed in a porcelain crucible with about 10 grams of 60-mesh iron filings, and the mixture covered with about 5 grams of 30-mesh filings. Two grams of the ore may be taken for the assay if less than 1 per cent. of mercury is present, 1 gram if the ore contains between 1 and 2 per cent. of mercury, and so on. The crucible is placed on a piece of tin-plate, cut so as to localise the heat round the crucible bottom. A piece of perfectly flat, annealed silver-foil, weighing from 2 to 6 grams, is placed over the crucible, and a second piece of foil slightly larger than the first is placed on it. Above the second cover and resting on it is placed a round copper vessel having a flat bottom and provided with inlet and outlet tubes, through which a supply of water is passed to keep the covers cool. The crucible is now heated by means of a small flame for about twenty minutes, care being taken that only the bottom of the crucible becomes red hot. After fifteen minutes' further cooling, the foil on which the mercury has collected is removed, carefully dried, and weighed. Tarry substances, if present, may be washed off the foil with a little alcohol. A weight may be placed on the cooling apparatus to ensure contact of the foil with the crucible top all the way round.

W. P. S.

[Qualitative] Separation of Metals of the Ammonium Sulphide Group. WERNER DAITZ (*Zeit. anal. Chem.*, 1906, 45, 92—95).—A somewhat adverse criticism of the scheme proposed by Boetticher (*Abstr.*, 1904, ii, 293).

L. DE K.

Behaviour of Ferric Chloride in the Zinc "Reductor." D. L. RANDALL (*Zeit. anorg. Chem.*, 1906, 48, 389—392).—The "reductor" consists essentially of a column of amalgamated zinc, and is employed in iron analysis for the rapid reduction of ferric to ferrous salts, the latter being subsequently titrated with permanganate. It is usually assumed that the method can only be used for the reduction of ferric sulphate, but the author shows that accurate results are also obtained with the chloride if some manganous sulphate is added and the solution sufficiently diluted. A slight excess of hydrochloric acid does not interfere with the accuracy of the method (compare Shimer, *Abstr.*, 1900, ii, 50).

G. S.

Diphenylcarbohydrazide [Diphenylcarbazine] as Indicator in the Titration of Iron with Dichromate. LEOPOLD BRANDT (*Zeit. anal. Chem.*, 1906, **54**, 95—99).—A preliminary communication. The ferrous solution, which should contain 0.2—0.7 gram of metal and from 60—80 c.c. of hydrochloric acid of sp. gr. 1.12, is added to 1500 c.c. of water containing 100 c.c. of Reinhardt's manganese solution [6 kilos. manganous sulphate, 33 litres dilute sulphuric acid (1 : 3), 3 litres phosphoric acid of sp. gr. 1.7, water up to 60 litres]. Five c.c. of an indicator, prepared by dissolving 0.1 gram of diphenylcarbazine in 35 c.c. of strong acetic acid and diluting to 100 c.c., are added, and standard dichromate is run in until the liquid turns violet.

L. DE K.

Separation of Tungsten and Tin. EDUARD DONATH (*Zeit. angew. Chem.*, 1906, **19**, 473—474).—A reply to Angenot on the estimation of tungsten in presence of tin (*ibid.*, 140).

The author prefers his own process. The mixed oxides are ignited with zinc dust in a closed crucible for fifteen minutes. When cold, the mass is heated with dilute hydrochloric acid (1 : 2) until no more hydrogen is evolved. Potassium chlorate is now carefully added until the blue colour has changed to pure yellow. The whole is diluted with, at least, $1\frac{1}{2}$ volumes of water, and after twenty-four hours the tungstic acid is collected, washed first with water containing a little nitric acid, and then with solution of ammonium nitrate. It is, finally, ignited and weighed. The tin may be recovered from the filtrate in the usual manner as sulphide.

L. DE K.

Estimation of Silver and Gold. CARL GOLDSCHMIDT (*Zeit. anal. Chem.*, 1906, **45**, 87).—Silver is precipitated quantitatively when its solutions are boiled with cobalt foil. In the same manner, gold may be precipitated by nickel foil. It is interesting to notice that nickel and cobalt serve as catalysts for gold and silver.

L. DE K.

New Method for the Estimation of Metals (especially Gold and Palladium) by means of Conductivity Measurements. JULIUS DONAU (*Monatsh.*, 1906, **27**, 59—70).—When a dilute solution of gold acidified with hydrochloric acid is reduced by means of carbon monoxide, its electrical conductivity increases considerably. The increase in the conductivity is not exactly proportional to the quantity of gold originally present in the solution, and for a given gold concentration it depends on the acidity of the solution. The following relationship has been deduced from a series of measurements. If z denote the number of milligrams of gold in 100 c.c., $x \cdot 10^{-4}$ the increase in the conductivity of the solution after reduction, and $y \cdot 10^{-4}$ the original conductivity, then $z = 1.76x - 0.0237xy + 0.0138x^2 - 0.00111x^2y + 0.000738xy^2$. Small quantities of foreign substances have no appreciable influence on this relationship.

Palladium can be estimated similarly, and in this case the increase in the conductivity or reduction is proportional to the concentration of the palladium, and is almost independent of the acidity of the solution. The increase in the conductivity multiplied by 1.21×10^{-4} gives the

number of milligrams of metal in 100 c.c. Solutions containing as little as 0.0005 per cent. of the metals can be examined by the author's method. The mean error is about 1 per cent. H. M. D.

Estimation of Organic Matters in Water. FRANZ UTZ (*Chem. Zeit.*, 1906, 30, 299—300).—The water is allowed to settle and then filtered through a Neubauer-crucible. The filtrate is tested for oxidisable matters as usual.

The suspended matters may be washed, dried, and weighed and, if desired, tested chemically and microscopically. L. DE K.

Use of Methyl Sulphate in the Estimation of Tar Oils in Admixture with Resin Oils or Mineral Oils. EDUARD VALENTA (*Chem. Zeit.*, 1906, 30, 266—267).—An accurately measured quantity of the tar oil is shaken in a graduated tube with twice its volume of methyl sulphate, which dissolves the true tar oils, but leaves behind any mineral oil or resin oil, the volume of which may then be read off. On heating the solution with aqueous sodium hydroxide, the solvent is decomposed and the tar oils are liberated, and may be weighed as a check.

Should the sample contain ordinary fats or resin, it must first undergo a preliminary treatment with alcoholic alkali.

On shaking fatty oils (olive oil, almond oil) with methyl sulphate, some of the latter dissolves in the oil. When using an equal volume of solvent, "pinolin" and oil of turpentine dissolve to the extent of about 30 per cent.; "pinolin" colours the solvent orange. Moreover, "pinolin" causes no rise in temperature, but with turpentine an appreciable elevation of temperature is noticed. L. DE K.

[The Bromine Absorption of] Commercial Oil of Turpentine. WILHELM VAUBEL (*Zeit. öffentl. Chem.*, 1906, 12, 107—108).—The bromine absorption of oil of turpentine is most conveniently estimated as follows: from 1 to 2 grams of the sample are dissolved in chloroform, about 100 c.c. of water, 5 grams of potassium bromide, and 10 c.c. of concentrated hydrochloric acid are added, and then a standardised potassium bromate solution is run in until a yellow coloration is obtained. The solution of the bromine in the chloroform enables the end-point to be ascertained readily. The bromine is absorbed rapidly by the turpentine at the beginning of the titration and more slowly afterwards, a persistent coloration being obtained usually in the chloroform within half an hour. Genuine oils of turpentine have a total bromine absorption (substitution and addition) of from 220 to 230, whilst the absorption of substitutes for this oil falls as low as 16, especially of those which do not contain pinene. W. P. S.

Detection and Estimation of Nitrotoluene in Nitrobenzene and of Toluene in Benzene. PAUL N. RAIKOW and FRL. E. ÜRKEWITSCH (*Chem. Zeit.*, 1906, 30, 295—296).—A mixture of 1 c.c. of light petroleum (gasolin), 0.5 gram of powdered sodium hydroxide, and a small drop of pure nitrobenzene remains colourless, but with nitrotoluene a yellowish-brown coloration is obtained. A fair idea may

be obtained as to the amount of nitrotoluene in a sample of commercial nitrobenzene by comparing the colour with that generated from a mixture of known composition.

To apply the test to benzene containing toluene, this must first be nitrated in the usual manner. L. DE K.

New Colour Reaction of the Cholesterols. D. OTTOLENGHI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 44—47).—The author has submitted a number of cholesterols and phytosterols to Neuberg and Rauchwerger's colour test (Abstr., 1905, ii, 122), which consists in treating an alcoholic solution of the substance first with either rhamnose or 4-methylfurfuraldehyde and then with concentrated sulphuric acid. Contrary to the results of these authors, it is found that this test does not afford a means of distinguishing the cholesterols from the phytosterols, the differences between the colours obtained in the two cases being only small. It appears probable that, under perfectly similar conditions, identical results would be obtained with the two classes of compounds. T. H. P.

Gravimetric Estimation of Sugar by means of Fehling's Solution. W. KELHOFER (*Zeit. anal. Chem.*, 1906, 45, 88—91).—A table giving the weight of invert sugar corresponding with amounts of cuprous oxide ranging from 10 to 485 mg. The corresponding amounts of metallic copper are also given. L. DE K.

Detection and Estimation of Trehalose in Plants [Fungi] by means of Trehalase. P. HARANG (*J. Pharm. Chim.*, 1906, [vi], 23, 16—20. Compare Bourquelot and Hérissé, Abstr., 1905, ii, 113).—Trehalose is extracted from a weighed quantity of the fresh fungus by comminuting this and macerating it in successive portions of boiling alcohol. The greater part of the solvent is distilled off from the extract and the syrupy residue poured into alcohol. The decanted liquid is evaporated to dryness at the atmospheric temperature under reduced pressure and the residue dissolved in water, saturated with thymol. In one portion of this liquid, the reducing and rotatory powers are determined. A second portion is treated with trehalase, prepared from *Aspergillus niger*, and, after the action of the enzyme has ceased, the reducing and rotatory powers are determined in this portion. Comparison of the two sets of data enables conclusions to be drawn as to the amount of trehalose, if any, present. *Clitocybe nebularis* was found to contain 9.443 grams of trehalose per kilogram of the fresh fungus. T. A. H.

Lignification. OTTO LINDE (*Arch. Pharm.*, 1906, 244, 57—62).—Concentrated sulphuric acid diluted with half its weight of water, or concentrated hydrochloric acid, colours the wood of *Coniferae* and of some other trees first yellow, finally green, the coloration being removed by water; other woods are coloured first yellow, finally brownish-green.

Wood is coloured violet when it is dipped in essential oil of myrrh, half-dried, and then immersed in the acid.

Wood is coloured indigo-blue by a mixture of amyl alcohol (free from furfuraldehyde) and concentrated sulphuric acid which has been heated until evolution of gas begins and then cooled. The red colour which this mixture gives to filter-paper is quite independent of the cellulose; it is due to the action of air on the mixture. C. F. B.

Estimation of the Carbonyl Group in Aldehydes, Ketones, &c. Modification of the Strache Method. WATSON SMITH, jun. (*Chem. News*, 1906, 93, 83—84).—In the present modification of Strache's method (compare Abstr., 1892, 546, 1530; 1893, ii, 560), a current of carbon dioxide is employed to drive the nitrogen evolved into a Schiff apparatus for measurement, any absorption of carbon dioxide by the Fehling solution being prevented by a floating layer of paraffin, whilst the benzene liberated is removed by the use of a mixture of sulphuric and nitric acids in a bulb-absorption apparatus or other means. D. A. L.

Testing Formaldehyde Pastilles. ERNST RÜST (*Zeit. angew. Chem.*, 1906, 19, 474).—These pastilles, much used for disinfecting purposes, should contain 95—97 per cent. of solid formaldehyde (trioxymethylene), which may be estimated by the author's process (*ibid.*, 138).

The average weight of one pastille should be about 1 gram. They should be entirely soluble in 100 c.c. of boiling water, and the solution should be neutral to phenolphthalein. When ten pastilles are heated in a platinum dish until they take fire, they should entirely burn, leaving at most about 0.1 per cent. of charred residue. The odour of the combustion fumes should be noticed. On further heating, not more than 0.08 per cent. of ash should be left. L. DE K.

Estimation of Small Quantities of Benzaldehyde. HENRI HÉRISSEY (*J. Pharm. Chim.*, 1906, [vi], 23, 60—65).—The author finds that the precipitation of benzaldehyde as the phenylhydrazone from its saturated solution in water is incomplete in the cold even after twenty-four hours, and the results obtained are too high if the mixture is left for several days at the atmospheric temperature. Good results can be obtained by heating the mixture for twenty minutes at 100°. This process has been successfully applied to the estimation of the amounts of benzaldehyde produced by the action of emulsin on the glucosides amygdalin, sambunigrin (Abstr., 1905, i, 912), and prulaurasin (this vol., i, 31). T. A. H.

Sources of Error in the Estimation of Acetone in Urine. L. BORCHARDT (*Beitr. chem. Physiol. Path.*, 1906, 8, 62—66).—Neuberg has shown that the estimation of phenol in the presence of sugar leads to erroneous results owing to the liberation by mineral acids from the sugar of substances which unite with iodine. The estimation of acetone in urine depends on the same principle as that of phenol, and the formation of substances of ketonic or aldehydic nature from sugar if this is present gives an unduly high result. Hence in diabetic urine the figures obtained are erroneous. What is the exact

nature of the substance formed from the sugar by the acid employed is uncertain. Exactly the same objection holds in regard to Geelmuyden's method, in which acetic acid is used. W. D. H.

Assay of Commercial Tartaric Acid. P. CARLES (*Bull. Soc. chim.*, 1906, [iii], 35, 171—174).—Attention is directed to a number of details of manipulation, which are of special importance in carrying out the estimation of tartaric acid in commercial mixed tartrates by the methods recommended by Goldenberg, Geromont and Co. (*Abstr.*, 1898, ii, 463, 545). T. A. H.

Estimation of Uric Acid in Birds' Urine. JULIUS KÓSSA (*Zeit. physiol. Chem.*, 1906, 47, 1—4).—In birds' urine the methods used for estimating uric acid in urine where it occurs in a dissolved condition are obviously not available. Good results are obtained by dissolving the urine in concentrated sulphuric acid and precipitating the uric acid by 90 per cent. alcohol. W. D. H.

Detection of Salicylic Acid in Alimentary Products. FELICE GORNI (*Rev. intern. Falsif.*, 1906, 19, 16—17).—The presence of lactic or tartaric acid inhibits the colour reaction between salicylic acid and ferric chloride. In testing wine, beer, or milk for salicylic acid, the author recommends a mixture of equal parts of ether and light petroleum as the best solvent for the salicylic acid. Lactic and tartaric acids are practically insoluble in this mixture. In cases where the amount of the latter acids greatly exceeds the quantity of salicylic acid, the residue obtained on evaporating the solvent should be dissolved in a little water and shaken out again with the ether-petroleum mixture. W. P. S.

New [Centrifugal] Method for Estimating Fat in Milk. Wendler's Method. VON KÜTTNER and ULRICH (*Zeit. öffentl. Chem.*, 1906, 12, 41—58).—Eleven c.c. of saline solution (containing tartrates, sodium chloride, and sodium hydroxide in certain proportions), 10 c.c. of milk, and 0.6 c.c. of isobutyl alcohol are placed successively in a butyrometer tube, the latter is closed with an india-rubber stopper, its contents mixed, and the tube then immersed in water at a temperature of 45° for a period of three minutes. After again shaking, the tube and its contents are subjected to centrifugal action and the quantity of separated fat read off after being once more brought to a temperature of 45°. The results obtained agree well with those yielded by Gerber's method for the same milk, as is shown by 360 comparative estimations. W. P. S.

Gerber's Salt-method [for the Estimation of Fat in Milk]. CARL BEGER (*Milchw. Zentr.*, 1906, 2, 120—123).—The method is a centrifugal one, the proteids, &c., of the milk being dissolved in a saline solution and the volume of the separated fat read off in a butyrometer tube. The saline solution is prepared by dissolving a certain weight of a salt (prepared by the inventor; the composition is not given) in 1 litre of water. Eleven c.c. of this solution, 10 c.c. of

milk, and 0.6 c.c. of *isobutyl* alcohol are placed successively in a butyrometer tube; the latter is closed by an india-rubber stopper and shaken for about half a minute. The tube is then immersed for three minutes in a water-bath at a temperature of 45°, again shaken, and the contents mixed by inverting the tube several times. The percentage amount of fat is read off at a temperature of 45° after the tube has been subjected to centrifugal action for three minutes. The results obtained agree well with those yielded by Gerber's "acid" method.

W. P. S.

The Influence of the Addition of Acetic Acid or Alcohol to Milk in the Estimation of the Total Solids. ADALBERT SEGİN (*Milchw. Zentr.*, 1906, 2, 115—119).—The practice of adding acetic acid to the weighed-out portion of milk to curdle the latter in order to hasten the time taken for the evaporation serves no useful purpose. In fact, the time taken to dry the solids to a constant weight is considerably lengthened, and the results obtained are about 0.1 to 0.4 per cent. too high. Alcohol is also an unsuitable curdling agent, small quantities not coagulating the milk and larger quantities increasing the yield of dry solids. There is a further objection to the use of alcohol in that, during the evaporation, it creeps up the sides of the basin and tends to cause loss.

W. P. S.

Quantitative Separation of Choline and Betaine. VLADIMÍR STANĚK (*Zeit. physiol. Chem.*, 1906, 47, 83—87. Compare this vol., ii, 60).—Betaine and choline, which often occur together in plants, both yield periodides, but the betaine periodide only forms crystals in acid solutions, whilst the crystals of choline periodide are obtained also in neutral and weakly alkaline solutions. The separation so effected is almost quantitative. A large number of other bases were investigated and many yield brown precipitates on similar treatment, but betaine, choline, and neurine hydrochlorides are the only ones that yield crystals.

W. D. H.

Estimation of Urea. BORIS GLASSMANN (*Ber.*, 1906, 39, 705—710).—The author describes a modification of the Liebig-Pfűger method of estimating urea in urine. An excess of standard mercuric nitrate is added to the urine after removal of sulphates, phosphates, and halogens, and the mixture nearly neutralised by sodium carbonate; the urea is precipitated, whilst the filtrate is acidified by nitric acid and the excess of mercury in it estimated, according to Rupp and Krauss' method (*Abstr.*, 1902, ii, 475), with ammonium thiocyanate, using ferric alum as an indicator. For the success of the method, the following conditions are necessary. The urine must contain traces only of proteids; it must not be undergoing alkaline fermentation; it must contain neither leucine nor tyrosine; if alkaline chlorides, bromides, or iodides or benzoic, hippuric, or salicylic acids are present, these substances must first be removed; the urine must not be too strongly coloured.

A. McK.

Assay of the Alkaloids of Javanese Coca. ANNE W. K. DE JONG (*Rev. trav. chim.*, 1906, 25, 1—6. Compare Abstr., 1905, ii, 778).

—The author states that Garsed's two processes for the assay of "crude cocaine" (Abstr., 1904, ii, 100) are unsatisfactory, the first because it is not certain that cinnamylcocaine is the only alkaloid in the crude cocaine, which is oxidised by potassium permanganate, and the second because the amount of bromine absorbed by cinnamic acid varies with the solvent used. The author proposes to make the assay as follows: a weighed quantity of the crude alkaloid is submitted to hydrolysis by baryta water. The insoluble matter formed in this process consists of undecomposed alkaloids, barium δ -isoatropate, and impurities; the two former are dissolved out by dilute hydrochloric acid, and the residue (impurities) is filtered, dried, and weighed. The δ -isoatropic acid is extracted from the solution in dilute hydrochloric acid with ether, dried, and weighed, and the result used to calculate the amount of δ -isoatropylcocaine present. The "undecomposed alkaloids" are estimated by rendering the liquid alkaline with ammonia and extracting with ether.

From the solution in the excess of baryta water, the benzoic, cinnamic, and ϵ -isoatropic acids are obtained by acidifying with dilute sulphuric acid and extracting with ether. They are then weighed as the mixed barium salts. From the mixed regenerated acids, ϵ -isoatropic acid is isolated by means of its slight solubility in warm water, and is dried and weighed. Cinnamic acid is estimated in the filtrate by conversion into the barium salts, dissolving these in hydrochloric acid, adding excess of bromine dissolved in carbon tetrachloride, and determining the bromine remaining uncombined after twenty-four hours. Benzoic acid is estimated by difference.

The excess of sulphuric acid added to the original solution is removed by adding baryta water, and the resulting excess of baryta by carbon dioxide. The filtrate is then concentrated and acidified with hydrochloric acid, and the precipitated γ -isoatropic acid is weighed. The residual liquid is evaporated to dryness and weighed. The barium in this residue is estimated as the sulphate, the ψ -tropine by rendering alkaline and extracting with chloroform, and the ecgonine by difference.

The results obtained by the analysis by this process of two Javanese "crude cocaines" are given in the original. T. A. H.

Colour Reactions of Proteids, Indole, and Scatole with Aromatic Aldehydes and Nitrites. F. A. STEENSMA (*Zeit. physiol. Chem.*, 1906, 47, 25—27).—The reactions described are mainly confirmatory of Rohde (Abstr., 1905, i, 618). A 2 per cent. solution of *p*-dimethylaminobenzaldehyde in 96 per cent. alcohol gives on boiling with proteid solution and 25 per cent. hydrochloric acid a red coloration; this changes to blue on the addition of a few drops of a 0.5 per cent. solution of sodium nitrite in water. The blue colouring matter is insoluble in chloroform; some proteids only give the last part of the reaction. Gelatin gives no reaction. The tryptophan group is considered by Rohde to be the cause of the reaction. Indole gives a red, changed to a deeper red by the nitrite. Scatole gives a bluish-violet, changed to deep blue by the nitrite; this is soluble in chloroform. If a 5 per cent. solution of vanillin in 96 per cent. alcohol is

used instead, proteid gives a red changed to blue by the nitrite ; indole gives an orange-red unchanged by the nitrite ; scatole gives a reddish-violet changed to bluish-violet by the nitrite.

If proteid is boiled with solid *p*-nitrobenzaldehyde and hydrochloric acid, a green coloration is produced ; this changes to dark blue on the addition of nitrite. Indole and scatole do not give any reaction with this reagent.

W. D. H.

Assay of Pepsin by the Biuret Reaction. WILLIAM B. COWIE and WILLIAM DICKSON (*Pharm. J.*, 1906, 221—223).—The value of pepsin depends on the amount of albumin it is capable of converting into peptone in a given time. On this fact, the authors have founded a colorimetric method based on the well-known biuret reaction for testing the relative power of samples of commercial pepsin. Briefly, the method is as follows ; for minute details, the original paper should be consulted. One gram of albumin is peptonised in the usual manner with 0.25 gram of pepsin in presence of 25 c.c. of *N*/10 hydrochloric acid. The resulting liquid is saturated with zinc sulphate, mixed with a few drops of dilute sulphuric acid, and boiled. When cold, 5 c.c. of the filtrate are placed in a Nesslerising tube, 15 c.c. of water and 1 c.c. of a 0.5 per cent. solution of copper sulphate are added, and then 80 c.c. of a 30 per cent. solution of sodium hydroxide. The red colour generated is now matched in a second tube containing 75 c.c. of water by means of a solution of potassium permanganate containing 0.04 gram of the salt per litre. The number of c.c. required are a measure for judging the peptonising power of the sample.

L. DE K.

Differentiation of Body Fluids containing Proteid. LEOPOLD VAN ITALLIE (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 8, 628—630).—Blood stains are tested for catalase with hydrogen peroxide after being heated at 63° for half an hour. Only blood from man or monkeys gives a positive test. Cow's milk is unable to decompose hydrogen peroxide after being heated at 63° for half an hour, whereas this property is retained by human milk after similar heating.

E. F. A.

The Intramuscular and Extramuscular Fat of the Principal Muscles of Horses and Oxen. RUDOLF HEFELMANN and PAUL MAUZ (*Zeit. öffentl. Chem.*, 1906, 12, 63—67).—The iodine number of the intramuscular fat of horses varies from 59.8 to 88.3, according to the condition of the animal, and that of the extramuscular fat from 58.2 to 90.7. The intramuscular fat of oxen gives iodine numbers from 43.7 to 59.2, whilst the extramuscular fat gives numbers varying from 41.1 to 50.1. The authors therefore conclude that the iodine number is of little use in detecting the presence of horse-flesh in other meats.

W. P. S.

General and Physical Chemistry.

Violet and Ultra-violet Absorption Spectra of Complex Copper Compounds. ALFRED BYK (*Ber.*, 1906, 39, 1243—1249).—It is shown that copper when introduced into the molecules of various aliphatic hydroxyl compounds, for example, tartaric acid, citric acid, and mannitol, acts as a bathochromic radicle, that is, it shifts the ultra-violet absorption bands slightly towards the red end of the spectrum. With aromatic compounds, for instance, the solution of copper salicylate in alkali, the shifting is extended into the visible part of the spectrum, and thus the solution is green in contradistinction to the bright blue colours of the solutions of the aliphatic compounds. Hydroxy-hydroaromatic compounds yield solutions of an intermediate bluish-green colour.

The absorption was examined quantitatively by passing the light from a spark between cadmium-zinc-lead electrodes, first through layers of the separate copper sulphate and sodium tartrate solutions placed one in front of the other, and then through the mixture; any increase in absorption in the second experiment is attributed to the formation of new complexes. The solutions were so selected as to contain molecular quantities of the different radicles in solution and so as to yield no precipitate when mixed. J. J. S.

Variations of the Absorption Bands of a Crystal in a Magnetic Field. JEAN BECQUEREL (*Compt. rend.*, 1906, 142, 775—777).—The absorption spectrum of xenotime, obtained by means of a Rowland grating, is modified when the crystal is placed in a magnetic field normal to the direction of the luminous rays, and the displacement of certain bands in the red and green is greater than the ordinary Zeeman effect observed in the spectra of metallic vapours. Further, the modification of the bands varies with the orientation of the optic axis of the crystal with respect to the magnetic field, thus a certain band in the green which is single and displaced towards the violet end of the spectrum when the optic axis of the crystal is normal to the magnetic field, becomes doubled when the optic axis is parallel to the magnetic field.

M. A. W.

Variations in the Absorption Bands of a Crystal in a Magnetic Field. JEAN BECQUEREL (*Compt. rend.*, 1906, 142, 874—876. Compare preceding abstract).—It is found that rays which are circularly polarised in the same direction are not all displaced in the same sense by a magnetic field. The explanation suggested is that certain bands correspond with vibrations of positively electrified particles, others with those of electrons. H. M. D.

Luminescence of Certain Organic Compounds between +100° and -190°. PETER BORISSOFF (*J. Russ. Phys. Chem. Soc.*, 1905, 37, ii, 249—346).—In order to ascertain the influence of temperature on phosphorescence and the relation between the latter and

fluorescence, the author has measured : (1) the intensity, colour, and duration of the phosphorescence of a large number of organic compounds at various temperatures from $+100^{\circ}$ to -190° ; (2) the phosphorescence of solutions of a number of organic compounds in alcohol, water, ether, benzene or chloroform; (3) the fluorescence of the substances in the solid state and in solution in the above-named solvents.

The phosphorescence experiments were carried out by first bringing the substance, enclosed in a thin-walled test-tube, to a definite temperature by immersion in a bath and then exposing for one second to the light of a Dubosc arc lamp, after which the substance was again plunged into the bath and its luminescence investigated.

The fluorescence was examined by : (1) observing with the naked eye the substance when illuminated by the voltaic arc; (2) spectroscopic observation of the fluorescence produced by ultra-violet rays; (3) Stokes's method; (4) observing with the naked eye the fluorescence produced by a ray of light after passing through a dark violet glass.

The results of the experiments are given in detail and lead to the following conclusions : (1) phosphorescence at low temperatures is a quite common phenomenon with organic compounds, only a few of which, for instance, fluorescein, *p*-nitroaniline, erythrosin, indigotin, alizarin, and cyanin, do not luminesce at the temperature of liquid air after exposure to the light of the voltaic arc. (2) Coloured organic compounds, such as nitro-compounds and aniline and other dyes, however, either do not luminesce or do so only very faintly; but solutions of certain colouring matters, for instance, rosaniline and fluorescein, luminesce quite strongly, although these compounds themselves exhibit either no or but faint luminescence. (3) Phosphorescence of organic compounds can be observed at much higher temperatures than is usually assumed. This is the case with many substances at -20° , and with some even at 100° . With most of the substances examined, luminescence commences at temperatures of from 50° to 150° below their melting points. (4) The most luminescent of the compounds examined are the organic acids, albumin, and certain alkaloids. (5) The predominating colour of the phosphorescence is green, the predominance being very marked. (6) At the temperature of liquid air, the duration of phosphorescence is independent of the duration of the previous illumination provided this exceeds one second. (7) In most cases, the duration of the phosphorescence diminishes linearly with increase of temperature, but in some instances the curves resemble hyperbola with the axis of temperature as their principal axis. (8) On raising the temperature, the phosphorescence becomes white with a blue tinge. (9) The intensity and duration of phosphorescence are, in general, diminished by rise of temperature. (10) At the temperature of liquid air, alcoholic and aqueous solutions phosphoresce more, some considerably more, distinctly than do the dissolved substances. (11) On altering the concentration of solutions, the duration, colour, and intensity of the phosphorescence change but little. (12) The durations of phosphorescence with solutions in chloroform and benzene are identical with those of the solvents themselves, but with solutions in alcohol, water, or ether this duration

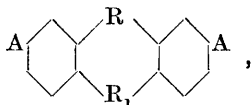
varies within wide limits. (13) With many substances, the light is unequally distributed over the surface of the phosphorescing material. With liquids at the ordinary temperature, the light is most intense at the bottom of the test-tube and near the meniscus, and with substances which crack on solidifying, along the fissures; when the substance remains transparent on freezing, this phenomenon is more marked than when the solid is opaque. This unequal surface-distribution of the light is also met with in the phosphorescence of crystalline powders, which exhibit bright star-like patches on a darker ground. (14) The colour of the fluorescence is generally distinct from that of phosphorescence and is mainly blue. (15) In fluorescence spectra, the predominant rays are those of medium refrangibility—between the *D* and *F* lines. (16) For the alcoholic solutions examined, the luminous parts of the fluorescence spectra become displaced towards the violet end. (17) Formic acid, 40 per cent. aqueous formaldehyde solution, acetaldehyde, acetone, phenol, tartaric acid, sodium potassium tartrate, dipentene, limonene, cocaine, and certain other compounds exhibit luminosity on change of temperature without previous exposure to light. (18) At low temperatures, resculin and barium platinocyanide retain in a latent form part of the energy absorbed at the temperature of liquid air and radiate it when the temperature rises. (19) Lactic acid, methyl acetate, aqueous solutions of malic, tartaric, and camphoric acids, and of cocaine hydrobromide and alcoholic α -bromopropionic acid, exhibit luminescence during the cleavage accompanying solidification.

T. H. P.

Fluorescence of Sodium Vapour caused by Monochromatic Light. ROBERT W. WOOD (*Chem. Centr.*, 1906, i, 899—900; from *Physikal. Zeit.*, 7, 105—106. Compare Abstr., 1903, ii, 621, and 1905, ii, 783).—In order to observe the fluorescence of sodium vapour in monochromatic light, a Heraeus quartz lamp is used, and the light emitted by cadmium analysed by means of a Fuess apparatus. The appearance of the fluorescent spectrum caused by the direct light of the cadmium tubes concentrated on the window of the sodium retort is entirely different from that formed when white light is used. The lines are sharp and brilliant and are not channelled. The violet cadmium line 4676 causes yellow and violet fluorescence, the blue line 4799 blue to yellowish-green, and the green line 5085 bluish-green to yellow.

E. W. W.

Fluorescence of Dyes. JULIUS FORMÁNEK (*Zeit. Farb. Ind.*, 1906, 5, 142—146, 164—169).—The author has studied the influence of structure on the power shown by certain dyes of fluorescing in solution. A large number of dyes is considered and the following conclusions arrived at. Only those dyes fluoresce when dissolved in water or ethyl or amyl alcohol which have a structure of the type



R denoting oxygen, sulphur, or nitrogen; *R*₁ carbon or nitrogen, and *A* a symmetrically situated auxochrome groups in a para-position to

the fundamental element; fluorescence persists if the hydrogen atoms of the amino-groups A A are replaced by alkyl or benzyl groups, but disappears if these are replaced by aromatic groups. The fluorescence varies with the character of the auxochromic groups and the nature of the radicles substituted into the two nuclei, and also depends on the solvent used.

W. A. D.

Theory of Optical Activity. CHR. WINTHER (*Zeit. physikal. Chem.*, 1906, 55, 257—280. Compare Abstr., 1905, ii, 493).—Attempts hitherto made to bring the optical activity of a substance into relation with its other properties have failed largely, owing, in the author's opinion, to the fact that in all such attempts only one property at a time has been considered in its bearing on the optical activity. In the present paper, an attempt is made to bring changes of rotation into connection with other molecular changes taking place simultaneously, namely, (1) changes of molecular volume, and (2) changes of molecular weight.

In certain cases, it appears that a change of rotation is determined by change of molecular volume or molecular solution volume alone. Substances belonging to this category are amyl itaconate, nicotine, and acetone solutions of the latter. There are also a number of substances investigated by Frankland, Patterson, and others, for which in the pure state the change of rotation with temperature is proportional to the change in molecular volume. These substances, however, have not yet been adequately studied in solution.

The author deals also with cases where the change of rotation $\Delta[\alpha]$ is determined not only by change in molecular volume Δv , but also by change in molecular weight (association). If Δm_1 is taken to represent the increase in the quantity of single molecules at the expense of double molecules for a rise of temperature ΔT , then a suitable formula to represent the variation in the rotation is $\Delta[\alpha] = K_1 \Delta m_1 + K_2 \Delta v$, or $\Delta[\alpha] = K_1 \Delta T / T_1 T_2 + K_2 \Delta v$, the latter equation being obtained from the former by putting $\Delta m_1 = k \Delta T / T_1 T_2$. The foregoing formulæ reproduce satisfactorily the change of rotation in the cases of ethyl and propyl tartrates, diethyl dibenzoyltartrate, and menthol, and it is noteworthy that in the last two cases even the observed maxima of rotation are reproduced by the formula. The foregoing formulæ may be extended to solutions of the substances in question, as is shown in detail for ethyl tartrate, the value of K_2 being the same as that obtained for the pure ester. If the formula is inverted, thus, $K_1 \Delta m_1 = \Delta[\alpha] - K_2 \Delta v$, it is seen that from the change of rotation and the change of molecular volume conclusions may be drawn as to the extent of association in these solutions.

The author discusses rotation dispersion from the standpoint of his theory, and concludes that substances exhibiting anomalous dispersion are substances the single and double molecules of which rotate the plane of polarisation in opposite directions and have different dispersions.

J. C. P.

Principle of Optical Superposition. M. A. ROSANOFF (*J. Amer. Chem. Soc.*, 1906, 28, 525—533).—It has been assumed by van't Hoff

that the optical activities of the asymmetric carbon atoms in a molecule are additive, the rotation due to any given atom being independent of the configuration of the groups attached to the other asymmetric carbon atoms. This assumption, which is known as the principle of optical superposition, has been considered to be strongly supported by the experimental work of Guey and Gautier (*Abstr.*, 1895, ii, 149) and Walden (*Abstr.*, 1895, ii, 149; 1896, ii, 138). In the present paper, the deductions which these authors made from the results of their experiments are criticised. It is affirmed that the results do not demonstrate the truth of the principle of optical superposition, but are rather in accord with the general proposition that the optical rotatory power of an asymmetric carbon atom depends on the composition, constitution, and configuration of each of the four groups. E. G.

Doppler Effect in Canal Rays and the Spectra of Positive Ions. JOHANNES STARK (*Chem. Centr.*, 1906, i, 891—892; from *Nachr. k. Ges. Wiss. Göttingen*, 1905, 459—471).—The positive ions of a chemical element can emit the line spectra of the element. Since Wien has shown that the canal rays consist of positive ions or atomic groups having great velocity, it follows that a portion of the spectrum emitted by a gas under the influence of the rays must consist of lines and that all the lines must show the Doppler effect. A band spectrum which does not give the Doppler effect is caused by the combination of the positive ions with the negative electrons of the ionised gas, and the velocity is not then so great as that of the canal rays. A band spectrum together with a line spectrum has been observed in the case of hydrogen and nitrogen. The Doppler effect is also shown by the series lines of the hydrogen spectrum, but not by the band spectrum. The line $\lambda = 3995\cdot3$ of the nitrogen spectrum gives the Doppler effect, but the band spectrum, even when the velocity of the canal rays is great, does not. The Doppler effect is also shown to a slight extent by the mercury lines $5461\cdot0$, $4358\cdot6$, $4046\cdot8$, and $3650\cdot3$, by the first subordinate series of sodium, and by the line $\lambda = 4044\cdot29$ of potassium. All the lines of the hydrogen series (H_α , H_β ,.....) are caused by the univalent positive hydrogen ions, and the principal and subordinate series of the alkalis and of mercury are similarly due to positive ions, but this does not hold in the case of the second hydrogen spectrum or the bands of the nitrogen spectrum. From the direction of the Zeeman effect shown by the series lines, it must be assumed that the centres of emission are negative electrons which are contained in the positive atom ions together with the positive charge; vibrations are set up by the electrons in the field of the positive charge and electromagnetic waves emitted.

The effect of pressure on the line series of elements is explained by the fact that the lines are caused by positive ions, and, inversely, it may be concluded that all the lines of an element which are displaced by pressure are due to positive ions. E. W. W.

Action of Light on Uranyl Acetate. ALEXIS BACH (*Ber.*, 1906, 39, 1672—1673).—When a 1·5 per cent. solution of uranyl acetate is exposed to direct sunlight for about 180 hours, no turbidity occurs;

when a current of carbon dioxide is passed through, the solution becomes turbid after thirty minutes. With equal illumination, concentration of uranyl acetate, and diameter of the tube used, the time when a perceptible turbidity appears in the solution is proportional to the height of the liquid in the tube used. The stronger the solution of uranyl acetate, the quicker is the action of light on it, a hot concentrated solution becoming turbid almost at once when exposed to light.

A. McK.

Increase of Conductivity of Dielectrics caused by the Action of Radium Rays. AUG. BECKER (*Chem. Centr.*, 1906, i, 890—891; from *Physikal. Zeit.*, 7, 107—108).—In reference to Righi's observation on the increase of conductivity of solid insulators caused by the action of radium rays (Abstr., 1905, ii, 793), the author points out that he had already conclusively proved this to be the case (*Ann. Physik*, 1903, [iv], 12, 124). The current is approximately proportional to the *E.M.F.*, and is independent of direction; it increases when the dielectric is exposed to the rays, and when withdrawn from their influence it gradually sinks to zero. The effect appears to be caused by the β -rays and cannot be ascribed, as Righi suggests, to bubbles of air contained in the dielectric (paraffin).

E. W. W.

Ionisation of Various Gases by the α -Particles of Radium. WILLIAM H. BRAGG (*Phil. Mag.*, 1906, [vi], 11, 617—632).—The range of the α -particle in a given gas is simply related to its constitution and is independent of temperature and pressure. The stopping power of a gas, in fact, is nearly proportional to the square root of its molecular weight (w), although more exactly it may be set equal to $a\sqrt{w} + bw$, where the second term is small compared with the first. The total ionisation of a gas, on the other hand, is not simply dependent on the weights of its component atoms: molecular structure counts for something. The author considers that his experiments indicate a secondary ionisation within the molecule itself.

J. C. P.

Radiations emitted by Polonium and Radiotellurium. P. EWERS (*Chem. Centr.*, 1906, i, 1084; from *Physikal. Zeit.*, 7, 148—152).—A somewhat complicated method for examining the radiations emitted by polonium and radiotellurium is described. A copper plate which is covered with polonium and placed in a very high vacuum is in contact with a second plate connected with a quadrant electrometer. Negative electrons are removed by means of a magnetic field. From the arrangement of the experiment, it appears improbable that both sets of particles can receive their charges in the gaseous space. From the effects produced by magnetic and electric fields, the velocity of the negative particles has been calculated to be 3.25×10^8 cm. per second, and the ratio e/m as 1.48×10^7 absolute units. Each square centimetre of the polonium preparation which was used was found to emit 5.1×10^7 α -particles per second, and the whole of the helium formed in a year would be practically too small to be detected.

E. W. W.

Time Constant of Polonium. MARIE CURIE (*Chem. Centr.*, 1906, i, 1225; from *Physikal. Zeit.*, 7, 180—181. Compare this vol., ii, 143).—Meyer and von Schweidler (*Sitzungsber. Akad. Wiss. Wien.*, Febr. 1906) have recently prepared a specimen of radioactive bismuth which has been found to consist of radium D, E, and F. The polonium prepared by the author, however, only contains rays which are readily absorbed, and is therefore free from radium D. Radium D is separated from the pitchblende together with lead and the polonium is separated from lead by repeated fractional precipitation from the solution in nitric acid by means of water. The absence of radium D is also shown by the fact that polonium preparations which were originally strongly active had become completely inactive in six years. The activity of the lead, however, which had been separated from the blende and contained radium D, E, and F in radioactive equilibrium, remained constant for years. E. W. W.

A New Product from Actinium. OSKAR HAHN (*Ber.*, 1906, 39, 1605—1607. Compare *Abstr.*, 1905, ii, 497).—A product has been obtained from actinium which corresponds with the radiothorium from thorium, and is therefore termed *radioactinium*. It emits α -rays, its activity decreases to half its initial value in some twenty days, and at the same time produces actinium X, which, in its turn, attains the half value in 10.2 days. The separation of radioactinium from an actinium solution is effected by carrying it down with some fine precipitate which settles slowly, one of the best precipitates being finely-divided sulphur obtained by adding a small amount of a sodium thiosulphate solution to a solution of an actinium salt strongly acidified with hydrochloric acid. The greater part of the actinium and actinium X remains in solution; the precipitate is strongly radioactive, but emits α -rays only; the activity tends to increase and attains a maximum value after about three weeks, when it is two to three times as active as when freshly prepared. It then decreases, and at the end of twenty days has attained the half value. The activity due to β -rays and to emanation also increases and then decreases in much the same manner as that due to the α -rays. The increase is attributed to the formation of actinium.

Actinium itself, free from radioactinium and actinium X, gives practically no α - or β -rays, but rapidly increases in activity and reaches a maximum at the end of four months.

When actinium is dissolved in hydrochloric acid, a minute quantity of insoluble matter is left which contains radioactinium. J. J. S.

New Element presenting the Radioactive Characters of Thorium. G. A. BLANC (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 328—335. Compare *Abstr.*, 1905, ii, 221 and 786).—From the deposits of the springs of Echaillon and Salins-Moutiers in Savoy, the author has separated a strongly radioactive preparation which is similar to thorium, but cannot be identical with thorium X, since its activity does not diminish as time increases, but increases to a constant maximum value. Neither is the activity due to actinium or radium, but it must emanate from a new element which is similar to

thorium, and is probably the one present in thorianite. The value of λ in the equation $I_t = I_0 e^{-\lambda t}$, taking one hour as the unit of time, is 0.00696 for thorium X, and 0.0070 for the deposits examined by the author. That the activity is due to an element resembling thorium and not to the latter itself is shown by the preparation of thorium, which is completely inactive. T. H. P.

Radioactivity of the Springs of Fiuggi, near Anticoli. RAFFAELLO NASINI and MARIO G. LEVI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 307—308).—Preliminary examination of the waters of Fiuggi shows that these are the most highly radioactive of Italian waters. T. H. P.

Radioactivity of Springs of Potable Waters. F. DIENERT (*Compt. rend.*, 1906, 142, 883—885. Compare this vol., ii, 211).—The waters of the springs feeding the river Vanne show the same activity as those feeding the Avre; they are more active than those which supply the Loing and the Lunain, but much less so than those supplying the Dhuys. There is a considerable difference in the activity of spring waters originating in the same geological formation, and no apparent relationship exists between the radioactivity and the electrical conductivity. Radium was absent from all the waters examined.

H. M. D.

Chemical Action of the Silent Discharge. WALTHER LÖB (*Zeit. Elektrochem.*, 1906, 12, 282—312).—Full details of the experiments described previously (this vol., ii, 43), together with the results of later experiments, are given. Traces of ozone and considerable quantities of hydrogen peroxide are found among the products obtained from moist carbon dioxide when a continuous current and the ordinary hammer make and break are used, but when an alternating current is passed through the primary circuit of the induction coil these products are absent. It is probable that ozone is the first product, and that the hydrogen peroxide is formed by its action on hydrogen, $2\text{H}_2 + 2\text{O}_3 = 2\text{H}_2\text{O}_2 + \text{O}_2$. Formaldehyde is always formed in small quantity by the interaction of hydrogen and carbon monoxide, the hydrogen being formed by the reaction $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$. By starting with a mixture of moist carbon monoxide and hydrogen, much larger quantities of formaldehyde are obtained, and also glycolaldehyde, $\text{OH}\cdot\text{CH}_2\cdot\text{CHO}$, which appears to be formed by polymerisation of formaldehyde. In the previous experiments (with carbon dioxide and alcohol), the aqueous solution of the product of the reaction was evaporated and the glycolaldehyde polymerised to β -acrose. The author has found, however, that the osazone of glycolaldehyde is precipitated from the aqueous solution itself, and that the sugar is not a primary product of the reaction.

Methane is always formed in small quantities from mixtures of gases containing carbon monoxide and hydrogen. Methane and carbon monoxide give acetaldehyde, $\text{CO} + \text{CH}_4 = \text{CH}_3\cdot\text{CHO}$, but the reduction of acetaldehyde to alcohol by combination with hydrogen under the influence of the silent discharge has not yet been realised.

The vapour of dry ethyl alcohol decomposes mainly into acetaldehyde and hydrogen, $C_2H_5 \cdot OH = C_2H_4O + H_2$; methane, ethane, and ethylene are also formed in moderate quantity.

The vapour of dry acetaldehyde decomposes mainly into methane and carbon monoxide. In presence of water, the other products which arise from its reaction with carbon monoxide are produced. The vapour of acetic acid appears to decompose primarily into methane and carbon dioxide. A large number of experiments with a mixture of carbon dioxide and alcohol vapour is described. The sugar previously obtained is shown to be formed by the polymerisation of glycol-aldehyde.

T. E.

Galvanic Cells produced by the Action of Light. II. Chemical Statics and Dynamics of Reversible and Irreversible Systems under the Influence of Light. MEYER WILDERMAN (*Proc. Roy. Soc.*, 1906, A, 77, 274—276).—An outline of what has been done in continuation of earlier work (*Abstr.*, 1905, ii, 499). Further evidence has been obtained showing that in homogeneous systems, under the action of light, chemical equilibrium and velocity of chemical reaction are subject to the laws of mass action.

J. C. P.

Movements on Mercury of Crystals while Dissolving due to Electro-capillarity. ALFRED THIEL (*Zeit. Elektrochem.*, 1906, 12, 257—259).—Crystals of potassium permanganate or dichromate placed on the surface of mercury under dilute sulphuric acid move backwards and forwards, or rotate whilst dissolving. The author connects this with the movements of a mercury surface in contact with an electrolyte which are produced by electrical means. In contact with most electrolytes, mercury assumes a positive charge which diminishes its surface tension; any cause which diminishes this charge increases the surface tension. If the diminution is local, it will produce a current of mercury on the surface, flowing from the place where the surface tension is smaller to places where it is greater. Since mercury is less positive towards a solution containing an oxidising agent, it appears that the movements of the crystals referred to may be explained in this way.

T. E.

Electrical Conductivity of Flames. J. F. DAVIDSON (*Chem. Centr.*, 1906, i, 890; from *Physikal. Zeit.*, 7, 108—112).—The conductivity of an ordinary Bunsen flame into which a solution of a salt is injected is determined by measuring the current produced by an *E.M.F.* of 400 volts. A D'Arsonval galvanometer is employed and a tube cooled by water serves as cathode. Even when the flame touches the anode, the result is not affected by the temperature, the superficial area, or the material of which the electrode is made. Although the temperature of the cathode is also immaterial, the strength of the current depends on its position and its superficial area. The use of an electrode which is contaminated with alkali, such as wood charcoal or dirty platinum foil, causes an immediate increase of current. In the inner cone of a pure flame, numerous ions are formed, which combine again, however, in the region immediately above. Larger currents

are obtained when the salt is placed on the cathode. An *E.M.F.* of 300 volts gives in the case of potassium chloride 1/40, of sodium salts 1/60, and of calcium salts 1/200 ampere (compare Wehnelt, *Ann. Physik*, 1904, [iv], 14, 425). Ionisation of the salt cannot occur unless the platinum cathode attains the temperature of the flame; the metal appears to retain the salt in a solid state for an extraordinarily long time. The current increases when the distance between the electrodes is decreased, and varies also with the position of the anode. When the anode is coated with the salt instead of the cathode, only about 1/4th of the current is obtained. A method of producing an alternating current is described, in which a platinum wire covered with calcium oxide is the cathode, and a platinum wire placed in the flame the anode. The strength of the current is greater the nearer the electrodes are to the region of ionisation, and is most affected by the position of the cathode. The temperature of the flame or the salt practically determines the conductivity of the flame. E. W. W.

Cause of the Conductivity of Air which has been in Contact with Phosphorus. RUDOLF SCHENCK, F. MIHR, and H. BANTHIEN (*Ber.*, 1906, 39, 1506—1521. Compare Harms, *Abstr.*, 1904, ii, 331; Meyer and Müller, *Abstr.*, 1905, ii, 141).—The authors have determined the conductivity of air and other gases by observing the rate of discharge of an electroscope charged with an *E.M.F.* of 200 volts; a diagram of the apparatus is given. The rate of discharge in strongly ozonised oxygen is not greater than in air: 1.5 volts in five minutes. The conductivity of ozone is not increased by contact with organic substances such as turpentine, amylene, eugenol, caoutchouc, silk, cotton-wool, linen, or wood, whilst that of air is not increased by contact with benzaldehyde, formaldehyde, acetaldehyde, methyl, ethyl, or amyl alcohol, methyl or ethyl ether, phenylhydroxylamine, indigo-white, pyrogallol, or triethylphosphine, or by the slow oxidation of sulphur or of bromoacetylene, which resembles phosphorus in that when slowly oxidised it shows the phenomenon of intermittent phosphorescence and forms a polymeride, tribromobenzene.

If the conditions are such that the oxidation of phosphorus is hindered, the increase in the conductivity of air or oxygen is correspondingly slight. Thus the conductivity of pure oxygen in contact with phosphorus under atmospheric pressure is much less than that of air under the same conditions. The conductivity of air which has been passed through turpentine, alcohol, mesitylene, ammonia, ethylene, or amylene is not increased by contact of the air with phosphorus, but, on the other hand, the conductivity is diminished only slightly if the process is reversed. Mixtures of oxygen with hydrogen or carbon dioxide give the same result as air. The conductivity of air or ozonised oxygen, but not of pure oxygen, is increased by contact of the gases with red phosphorus.

The authors conclude that the conductivity of air which has been in contact with phosphorus is connected with the presence of phosphorous oxide, and may be caused by the interaction of the trioxide and moisture to form phosphorous acid. The electroscope is discharged by phosphorous oxide at the rate of 40--50 volts in five minutes at

22.5°. The rate of discharge is diminished to 10 volts in five minutes if the air containing the trioxide is passed through a worm condenser cooled by ether and solid carbon dioxide. As determined by the dynamic method in a modification of Ramsay and Young's apparatus, the vapour tension of phosphorous oxide varies from 2.7 mm. at 22.4° to 50.8 mm. at 72.7°, 248.7 mm. at 88.6°, and 297.9 mm. at 91.2°. The rate of oxidation of phosphorous oxide was determined by sealing the liquid oxide in an atmosphere of dry oxygen in a flask fitted with a manometer, and observing the alteration in pressure. No oxidation takes place at 10°; at 40°, the rate of oxidation is proportional to the square root of the pressure of the oxygen. The surface tension of liquid phosphorous oxide has the temperature-coefficient 1.9—2.6 at temperatures between 34.3° and 109.4°, as determined by Ramsay and Shields' method; the specific conductivity is less than 1.2×10^{-7} at 25°, and the dielectric constant is 3.2 at 22°. G. Y.

Relation between Electrolytic Conduction, Specific Inductive Capacity, and Chemical Activity of Certain Liquids. JOSEPH H. MATHEWS (*J. Physical Chem.*, 1906, 10, 216).—Attention is called to certain numerical errors in the author's paper bearing the above title (this vol., ii, 3). L. M. J.

Bearing of Hydrates on the Temperature-coefficients of Conductivity of Aqueous Solutions. HARRY C. JONES (*Amer. Chem. J.*, 1906, 35, 445—450. Compare Jones and West, *Abstr.*, 1905, ii, 794).—It is shown that the conductivity of aqueous solutions of electrolytes increases with rise of temperature owing, in general, to an increase in the velocities of the ions, and that this increase in velocity is partly due to a decrease in the masses of the ions caused by the decreasing complexity of the hydrates formed around them. A number of examples are quoted which show that those substances which have equal hydrating power have approximately the same temperature-coefficients of conductivity, and that the greater the hydrating power of the electrolyte the greater is the temperature-coefficient of conductivity of the solution. It is also shown that the temperature-coefficients increase with the dilution, and that this increase is greatest for those substances which have large hydrating power. E. G.

Silver Derivatives of Acid Amides and Imides. II. HEINRICH LEY and KONRAD SCHAEFFER (*Ber.*, 1906, 39, 1259—1266. Compare *Abstr.*, 1902, i, 358).—Silver succinimide is best purified by recrystallisation from a dilute solution of succinimide, as it is slightly hydrolysed by hot water. Its aqueous solution gives the reactions for silver ions both with solutions of hydroxides and chlorides, and also has a slight alkaline reaction.

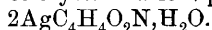
The electrical conductivity of its aqueous solution is far below that for silver acetate solution of the same concentration. Although the alteration in value of the conductivity resembles cases where slight hydrolysis occurs, it has been shown that in this case practically no hydrolysis takes place, since the conductivity remains almost the same when free succinimide is introduced into the solution.

The concentration of the silver ions in a saturated solution has been calculated as 7.7×10^{-3} from the conductivity. The concentration has been calculated from the *E.M.F.* of the following concentration cells :

Ag | Saturated solution of | $0.05N$ KNO_3 | $0.05N$ $KClAgCl$ | Ag = 0.353 volts
silver succinimide

Ag | Saturated solution of | $0.05N$ KNO_3 | $0.1N$ $AgNO_3$ | Ag = 0.075 ,,
silver succinimide

as 4.2×10^{-3} . The high value obtained by the conductivity method may be due to the formation of complex ions, $Ag(C_4H_4O_2N)_2'$. The silver salt contains water of crystallisation, probably



Electrical conductivity determinations of silver nitrite solutions gave numbers similar to those obtained by Niementowski and Roszkowski (Abstr., 1897, i, 340). The specific conductivity of a saturated solution at 25° is 0.00209 . The solubility is 0.0263 gram-mol. per litre, and the degree of ionisation of the saturated solution 0.59 . The solubility product $Ag^+ \times NO_2^-$ for silver nitrite at 25° is given as 2.4×10^{-4} (compare Abegg and Peck, Abstr., 1905, ii, 586). From the small dissociation of silver nitrite it is argued that the solution probably contains not merely the silver-oxygen derivative and its ions, but also the non-ionised silver-nitrogen derivative.

Experiments show that in dilute solutions of sodium nitrite the silver salt does not form complex salts to any appreciable extent.

Silver nitrite as a sparingly soluble salt behaves normally as regards the decrease of its solubility by the addition of one of its ions.

J. J. S.

Electric Measurements on Metals. CHARLES E. FAWSITT (*Proc. Roy. Soc. Edin.*, 1906, 25, 2—6).—There is in general a difference of potential between different varieties of the same metal, and when placed in a solution of one of its salts the amorphous phase is in general negative to the crystalline phase. The author's experiments with silver, gold, and platinum show that if two rods of either of these metals be softened by annealing, and one of them then hardened by polishing or hammering, the latter becomes the negative pole when the rods are placed in a solution of one of its salts or in other electrolytes.

L. M. J.

The Iodine and Ferric-ferrous Potentials. WILLIAM MAITLAND (*Zeit. Elektrochem.*, 1906, 12, 263—268).—The potential of an unalterable electrode in a solution containing iodine and iodine ions is expressed by $\epsilon = A + 0.02955 \log_{10} [I_2]/[I']^2$. The normal potential, A , may be defined as the potential in a solution which is normal with respect to iodine ions, (A_1) is saturated with iodine, and (A_2) contains 1 gram-molecule of iodine per litre. The two values differ by 0.0849 volt. The mean value of A_2 calculated from a large number of determinations is 0.3418 volt at 25° compared with the normal calomel electrode. The *E.M.F.*'s of cells made up of a platinum electrode immersed in a solution of ferrous and ferric nitrates and a normal

calomel electrode were also measured. The results are expressed by the formula $\epsilon \cong 0.460 + 0.0591 \log [\text{Fe}^{+++}]/[\text{Fe}^{++}]$. Owing to incomplete dissociation, there was some uncertainty about the concentration of the ions, especially in the more concentrated solutions. When a ferric salt and iodine ions or a ferrous salt and iodine are mixed together, equilibrium will be attained when the ratios $[\text{Fe}^{+++}]/[\text{Fe}^{++}]$ and $[\text{I}_2]/[\text{I}^-]^2$ are such that the corresponding potentials are the same. The authors show that this is actually the case, and that the reactions studied by Seubert and his students (Abstr., 1894, ii, 140 and 191; 1895, ii, 17, 111, and 395) may be treated quantitatively by means of the values above given. T. E.

Spontaneous Ionisation of Air and Other Gases. HANS GEITEL (*Chem. Centr.*, 1906, i, 1080; from *Ber. Deut. phys. Ges.*, 4, 23—38).—The ionisation of air increases slowly until a limiting value is attained. Cellar and stagnant air at a constant temperature gives values which are far higher than those of artificially prepared samples such as air from pores. It would thus appear that radioactivity is the cause of the ionisation. Extremely small traces of radium are distributed over the whole globe. An emanation which is identical with that of thorium is also frequently detected, although its origin is not proved. Since the emanations from thorium or actinium do not persist for long, they have hitherto only been found on the ground or in the air near it. The results of Elster and Geitel's experiments (*Physikal. Zeit.*, 6, 733) support the theory that the electrification of the air is due to these radiations. Precise measurements are rendered difficult by the persistent after-effects of radioactive preparations, and by the slight radioactivity induced in the instruments themselves. There is as yet no definite indication of the presence of other active emanations. Different metals ionise the air in their proximity in different ways, but it is uncertain whether the effect is due to radiation from the metals themselves or to their influence on the radiations which are already present; many observations, such as those of Wood and Campbell, support the former hypothesis. At temperatures below that at which the phenomenon of electric glow begins to be visible (about 450°), variation of temperature has no effect on the ionisation. The spontaneous ionisation of gases cannot yet be regarded as entirely due to radioactivity. E. W. W.

Accurate Measurement of Ionic Velocities with Applications to Various Ions. ROBERT B. DENISON and BERTRAM D. STEELE (*Phil. Trans.*, 1906, A, 205, 449—464).—Details are given of work already described (this vol., ii, 68). J. C. P.

Ions produced by Falling Liquids. E. ASELMANN (*Ann. Physik*, 1906, [iv], 19, 960—984).—Distilled water produces only negative ions, solutions of sodium chloride produce positive and negative ions simultaneously. Incidentally, the conclusion is reached that, to make a visible yellow coloration of a Bunsen flame for one second in a dark room, 1.5×10^{-8} milligrams of sodium chloride is sufficient. J. C. P.

Results and Problems of the Theory of Electrons. HENDRIK A. LORENTZ (*Arch. Néerland.*, 1906, [ii], 11, 1—52).—A lecture delivered before the Berlin Electrotechnical Society. J. C. P.

Action of Organic Colloids on the Electrolytic Deposition of Copper. ERICH MÜLLER and PAUL BAHNTJE (*Zeit. Elektrochem.*, 1906, 12, 317—321).—From an acid solution of copper sulphate containing gelatin, copper is deposited in a smooth form resembling the burnished metal. The result depends on the quantity of gelatin and on the current density. A solution containing 0.5 mol. of copper sulphate, 0.1 mol. of sulphuric acid, and 1 gram of gelatin per litre and a current density of 0.035 ampere per sq. cm. gives good results. The solution must be free from suspended particles. Albumin gives similar results. "Gum" and starch also affect the nature of the deposit, but only in more strongly acid solutions. None of the colloids tried have any effect on the deposit in alkaline (cyanide) solutions. The burnished deposits weigh more than the ordinary crystalline deposits and contain organic matter. The authors explain the influence of the colloids used by their known effect in retarding the coagulation of hydrosols by electrolytes. They suppose that metals are deposited at the cathode in the amorphous form, the colloids preventing the crystallisation of the deposit. This involves the assumption that the colloids migrate to the cathode under the influence of the current. They are able to show that this is the case with gelatin in acid solutions, but not in alkaline solutions. Albumin behaves in the same way. The difference between the behaviour of the colloids towards acid and alkaline copper solutions is thus accounted for. T. E.

Electrical Preparation of Colloidal Solutions. THE SVEDBERG (*Ber.*, 1906, 39, 1705—1714. Compare Abstr., 1905, ii, 817).—The spark discharge between zinc or aluminium electrodes immersed in *isobutyl* alcohol is far less efficient than the arc discharge in the production of colloidal solutions; hence the author considers that the success attending his second method (*loc. cit.*) is due to the formation of numerous small arc discharges between the loose particles of metal, resulting in very rapid pulverisation.

Colloidal solutions in ether are very unstable; numerous organic solvents were employed unsuccessfully, but anhydrous acetone, paraldehyde, and particularly propyl alcohol or *isobutyl* alcohol were found to give stable solutions. Stability is also conferred on a solution by the addition of a small quantity of a slightly dissociated electrolyte with a large positive ion of low mobility, for example, stable colloidal solutions were obtained in ether containing a few drops of bromobenzene. This phenomenon is in harmony with Billitzer's theory (Abstr., 1905, ii, 305). Low temperatures (-84°) are also favourable to increased stability.

An apparatus is described for the production of stable ethereal solutions, of colloidal sodium at the ordinary temperature, and of potassium, rubidium, and caesium at -84° . The greater the atomic weight of the alkali metal, the more the colour of its colloidal solution approaches the red end of the spectrum; moreover, the colour of the

solution is identical with that of the metal in the vaporous state. Numerous other metals have been obtained in colloidal solution in *iso*-butyl alcohol, and a tabulated statement of their colour and relative stability is given.

The pulverising action of the high tension arc discharge has also been utilised in the production of colloidal solutions of carbon, silicon, selenium (compare Müller and Nowakowski, this vol., ii, 18), and tellurium, and of certain minerals such as magnetic iron ore, copper glance, and molybdenum glance. An apparatus is described in which are obtained colloidal solutions in *isobutyl* alcohol of substances of very small conductivity, such as sulphur, red phosphorus, mercuric oxide, copper oxide, Prussian blue, &c. An attempt to obtain a colloidal solution of potassium permanganate resulted in the formation of colloidal manganic hydroxide.

C. S.

Magnetic Susceptibility of the Manganic Salts. R. H. WEBER (*Ann. Physik*, 1906, [iv], 19, 1056—1070).—The magnetic susceptibility of the manganic salts is considerably less than that of the manganous salts, and greater than that of the chromium salts. The susceptibility of the peroxide $\text{MnO}_2 \cdot \text{H}_2\text{O}$ dissolved in hydrochloric acid is approximately the same as that of the manganic salts.

J. C. P.

Quantitative Relation between the Specific Heats of a Gas and its Molecular Constitution. PHILIP BLACKMAN (*Chem. News*, 1906, 93, 145).—From the equation $C_p - C_v = R/J$, it follows that $\gamma = 1 + R/JC_v$. If the molecular condition of a gas is unaltered by a rise of temperature, the value of γ will decrease, for R is constant and C_v increases. The value of γ increases, however, with decreasing molecular complexity, so that in the case of a gas dissociating in stages the curve representing γ as a function of the temperature will exhibit an alternating series of maxima and minima.

H. M. D.

Relation between the Melting Point and the Coefficient of Expansion of the Solid Elements. H. F. WIEBE (*Ann. Physik*, 1906, [iv], 19, 1076—1078).—The relationship deduced by Panayeff (*Ann. Physik*, 1905, 18, 210) is not new (see Carnelley, *Abstr.*, 1879, 588; Pictet, *Compt. rend.*, 1879, 88, 855; Weber, *Ann. Physik*, 1905, [iv], 18, 868).

The author himself has shown previously (*Abstr.*, 1880, 783) that the heat necessary to raise the temperature of a gram atom of an element from the absolute zero to its melting point (T) is inversely proportional to its coefficient of cubical expansion (α). When this rule is combined with Dulong and Petit's law, it is found that $(\alpha T)^2 = \beta$, the coefficient of expansion for gases. This relationship is shown to be fulfilled, with fair approximation, in the case of some twenty elements.

J. C. P.

Course of Melting-point Curves for Compounds which are Partially Dissociated in the Liquid Phase, the Proportion of the Products of Dissociation being Arbitrary. JOHANNES J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 8, 699—714).—When two components form a compound, then the melting-point

curve of this compound will have a horizontal direction at the summit if there is but the slightest dissociation in the liquid phase. The slighter the dissociation of the compound, the sooner will the initial horizontal course pass into a descending course as excess of one component or the other is added. The author gives a fresh mathematical proof of these statements, and deduces formulæ for the course of the melting-point curve below the summit. J. C. P.

Dissociation of Fused Compounds. ROBERT KREMAN (Zeit. Elektrochem., 1906, 12, 259—263).—In a former paper (Abstr., 1905, ii, 76), the author drew the conclusion that the freezing point of an additive compound, which dissociates partially when fused, might be raised by the addition of one of its components. He now points out that this is not the case, the error being due to the approximate method employed to calculate the molecular composition of the mixtures. In reality, a depression of freezing point must always occur. The more accurate calculation shows that the degree of dissociation of the molecular compound of phenol and aniline is 25 per cent. (instead of 20 per cent.), whilst that of the compound of phenol and picric acid is 35 per cent. (instead of 27 per cent.). T. E.

Isothermal Distillation of Nitrogen and Oxygen and of Argon and Oxygen. JOHN K. H. INGLIS (Phil. Mag., 1906, [vi], 11, 640—658).—Isothermal distillations of mixtures of liquid oxygen and nitrogen have been carried out at 74.7° abs. and 79.07° abs., and the compositions of the liquid and vapour in equilibrium with each other have been determined. In order to secure this equilibrium, the vapour was circulated through and through the liquid until no further change took place in either. If R_v and R_l are the ratios of nitrogen to oxygen in the vapour and liquid respectively, and m is the molecular percentage of nitrogen in the liquid, then at 74.7° abs. $R_v/R_l = 6.60 - 0.028m$, and at 79.07° abs. $R_v/R_l = 5.48 - 0.0207m$, these equations reproducing the experimental results with close approximation. When the total pressure and the partial pressures of oxygen and nitrogen are plotted against the molecular composition of the liquid, the curves obtained, although they have only slight curvature, are certainly not straight lines. Further consideration of the relation of these partial pressures to composition shows that the solubility of nitrogen in oxygen is in accordance with Henry's law up to a molecular percentage of nearly 70, but that the value of the quotient concentration/pressure for oxygen varies in such a way as to indicate association of oxygen molecules when dissolved in nitrogen.

The vapour pressure of pure argon at 82.09° abs. is 411 mm., and when a little oxygen is added the vapour pressure rises to 420 mm. and remains at this value, in spite of continued addition of oxygen, so long as any solid argon is left. This saturated solution of argon in oxygen contains 92.7 per cent. argon by volume, and the vapour in equilibrium with it contains 97.8 per cent. of argon. J. C. P.

Modification of van't Hoff's Theory of the Depression of the Freezing Point. II. J. B. GOEBEL (Zeit. physikal. Chem., 1906, 55, 315—320. Compare Abstr., 1905, ii, 679).—Another satisfactory

formula connecting c' and Δ (see *loc. cit.*) is the following: $c' = 0.391\Delta + \Delta/(6.67 + 4.2\Delta + 9.2\Delta^2 - 8.4\Delta^3 + 3.4\Delta^4)$. The numerical coefficients in this formula are deduced from Raoult's measurements of the freezing point of sucrose solutions. When c' is calculated by the foregoing formula from the freezing-point depressions observed in solutions of sodium, potassium, and lithium chlorides and potassium bromide, values are obtained which are in harmony with Ostwald's dilution law.

J. C. P.

Molecular Condition of some Salts in Pyridine. PAUL WALDEN and MIECZYSLAW CENTNERSZWER (*Zeit. physikal. Chem.*, 1906, 55, 321—343).—The authors have made a fresh determination of the boiling-point elevation constant of pyridine, using phenanthrene, diphenylamine, and benzil as solutes, and find 27.1 as the mean value. The experiments show that this constant is extremely sensitive to traces of impurities in the pyridine, such as its higher homologues, and especially water. Schroeder's observation (*Abstr.*, 1905, ii, 306) that certain mercury salts produce a depression, instead of an elevation, of the boiling point of pyridine, is not confirmed, and it is shown that a small quantity of water in the dissolved salt may be the cause of such observed depression.

The influence of a number of salts on the boiling point of pyridine has been studied, and the results lead to a classification of the salts in two groups. On the one hand, mercuric chloride, bromide, iodide, and cyanide and ethyl mercuric chloride are found in concentrated solutions to have a molecular weight which is less than the normal value. On the other hand, the molecular weights of silver nitrate and tetraethylammonium iodide, dissolved in pyridine, are greater than the normal value, and in the case of the former salt i passes through a minimum value (about 0.75). For both classes of substances, the molecular weight in dilute solutions approximates to the normal value. These results are similar to those obtained with liquid sulphur dioxide as solvent (see *Abstr.*, 1902, ii, 245), and it is probable that in the present case also the somewhat abnormal results obtained are due to a co-operation of several factors, such as polymerisation of salt molecules and combination of solute and solvent. The part played by the last-mentioned factor is estimated quantitatively on the lines of Jones and Getman's hypothesis (see *Abstr.*, 1905, ii, 386, 710, 711). J. C. P.

Vapour Pressure in Equilibrium with Substances holding Varying Amounts of Moisture. FREDERICK T. TROUTON and Miss B. POOL (*Proc. Roy. Soc.*, 1906, A, 77, 292—314).—With the aid of special apparatus, the authors have estimated the amounts of water held by different fabrics under varying conditions of temperature and humidity. It is found (1) that the weight of water held by a given material is determined by the relative humidity alone, (2) that at any given temperature the amount of water held varies with the saturation according to a parabolic law, except in the neighbourhood of complete desiccation. The results are summed up in the comparison of two kinds of curves: (1) isohygrometric curves, that is, curves on the pressure-temperature diagram, so drawn that the pres-

sure is always a constant fraction of the saturation pressure; (2) "isoneric" curves or "isoneres," in which the pressure of vapour from a material holding a constant weight of water is plotted against temperature. It is found that the isoneres approximately coincide with the isohygrometrics. The same relation holds approximately in the case of sulphuric acid solutions.

J. C. P.

Trustworthiness of the Calculation of Heating Values of Fuels from Analyses. OTTO MOHR (*Chem. Centr.*, 1906, i, 960; from *Woch. Brau.*, 23, 76—78).—In calculating the heating values of fuels from analyses, the sulphur is especially a cause of uncertainty. The sulphur, which is present as sulphate, either remains in the ash or is given off as sulphur trioxide. Since iron pyrites forms ferric oxide or triferrous tetroxide, the weight of the ash includes the gain due to the oxygen, and the percentage of oxygen and nitrogen which is obtained by difference is consequently too low. In one case, the error due to this cause amounted to 147 units. The presence of carbonates interferes with the accurate determination of the carbon of the fuel, and the estimation of hydrogen is also subject to error when water is present, since it cannot be completely removed by heating at 106°. For these reasons, the calorific value of coals cannot be calculated with sufficient accuracy from the results of analysis.

E. W. W.

Thermochemical Investigation of the Decomposition of Organo-magnesium Ether Complexes by Water. WLADIMIR TSCHELINZEFF (*Ber.*, 1906, 39, 1674—1681. Compare Abstr., 1905, ii, 802; this vol., i, 241).—The author has measured the thermal effects produced by the decomposition by water of various organo-magnesium ether compounds in various indifferent solvents. The ether complexes first examined were prepared in two phases: magnesium, ethyl ether, and alkyl haloid were caused to interact in light petroleum, benzene, and hexane respectively by the author's catalytic method with a tertiary amine; the resulting solids were then acted on by an excess of ether. The thermal effects of the addition of water on the complexes thus prepared were contrasted with the effects on the corresponding complexes prepared according to Grignard's method and found to be very similar.

The action of water on the compounds, $\text{MgEtI}, 2\text{Et}_2\text{O}$;

$\text{MgPr}^a\text{I}, 2\text{Et}_2\text{O}$;

$\text{Mg}(\text{C}_4\text{H}_9)\text{I}, 2\text{Et}_2\text{O}$; $\text{Mg}(\text{C}_5\text{H}_{11})\text{I}, 2\text{Et}_2\text{O}$, prepared by both methods, was examined.

The conclusion is drawn that the ether complexes prepared by the author's catalytic method by aid of a tertiary amine on the one hand and by Grignard's usual method on the other are identical in structure.

A. MCK.

Thermochemical Investigation of the Decomposition of Organo-magnesium Compounds by Water. WLADIMIR TSCHELINZEFF (*Ber.*, 1906, 39, 1682—1685. Compare preceding abstract).—The author has studied the thermal effect produced by decomposing with water solutions of ether-free magnesium alkyl haloids in benzene

or in light petroleum. If the heat developed in the reaction $\text{RMgI} + 2\text{R}_2\text{O} = \text{R} \cdot \text{MgI} \cdot 2\text{R}_2\text{O}$ be t , and that by the reaction $\text{RMgI} \cdot 2\text{R}_2\text{O} + \text{Aq.} = \text{RH} + \frac{1}{2}\text{MgI}_2 \cdot \text{Aq.} + \frac{1}{2}\text{Mg}(\text{OH})_2 + 2\text{R}_2\text{O}$ be t_2 , whilst T' represents the heat evolved in the reaction $\text{RMgI} + \text{Aq.} = \text{RH} + \frac{1}{2}\text{MgI}_2 \cdot \text{Aq.} + \frac{1}{2}\text{Mg}(\text{OH})_2$, then $T' = t_1 + t_2$. From data quoted in this and in the preceding paper, this relationship is borne out by experiment. A. McK.

Heats of Formation of Magnesium Alkyl Halides from their Elements. Heat evolved in the Preparation of Magnesium Alkyl Halides. WLADIMIR TSCHELINZEFF (*Ber.*, 1906, 39, 1686—1690. Compare preceding abstracts).—The heats of formation of the compounds $\text{C}_2\text{H}_5\text{MgI}$, $\text{C}_3\text{H}_7\text{MgI}$, $\text{C}_4\text{H}_9\text{MgI}$, and $\text{C}_5\text{H}_{11}\text{MgI}$ from their constituent elements are calculated to be 60·7, 63·7, 72·5, and 72·6 Calories respectively.

The heat developed in the combination of magnesium and ethyl iodide is also calculated. If Thomsen's figure for the heat of formation of ethyl iodide from its elements be taken, then the value of Q in the equation $\text{Mg} + \text{C}_2\text{H}_5\text{I} = \text{C}_2\text{H}_5\text{MgI} + Q$ is +50·8 Cal., whereas if Berthelot's figures be taken, then $Q = +36\cdot0$ Cal. A. McK.

Organic Solvent and Ionising Media. III. Viscosity and its Relation to the Conductivity. PAUL WALDEN (*Zeit. physikal. Chem.*, 1906, 55, 207—249. Compare Abstr., 1904, ii, 227; this vol., ii, 149).—The author has determined the viscosity (η) at 0° and 25° of forty solvents, and finds that there is an obvious parallelism between the magnitude of the viscosity itself and that of its temperature-coefficient (α); the greater the viscosity, the greater is the temperature-coefficient of the viscosity. Indeed, for about half the solvents examined the relation $\eta_{25}/\alpha = 0\cdot43$ holds approximately. There is apparently no relationship between the viscosity and the association factor, the molecular volume, or the dielectric constant.

The viscosity is a markedly constitutive property, as may be seen from the following table, which gives the values of η_{25} for a number of solvents.

	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \\ \\ \text{CH}_3 \end{array}$	-CN.	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \\ \\ \text{Cl} \end{array}$	-NCS.	-NO ₂ .	-SNC.	-CO ₂ H.	-OH.
-CH ₃ ...	0·00256 (10°)	0·00316	0·00346	0·00387	—	0·00619	0·00719	(0·0113)	0·0058
-C ₂ H ₅ ..	0·00345	—	0·00413	0·00460	0·00618	—	0·00775	0·0103	0·0108
-C ₆ H ₅ ...	0·0140	—	0·0125	—	0·0139	0·0182	—	—	—

The viscosity of mixtures of (1) lactonitrile and acetonitrile, (2) acetone and methyl cyanoacetate, has been studied. In both cases the observed viscosity differs widely from the value calculated on the supposition that the mixed liquids are without mutual action.

Solutions of tetraethylammonium iodide and one or two ternary salts in several of the solvents have been examined, and it is found that when the solutions are dilute ($v > 200$) the values of η_0 , η_{25} , and α are practically identical with the corresponding values for the pure solvents. This being so, it is permissible to use the experimental data on viscosity obtained for the pure solvents in discussing the relationship between the conductivity and the viscosity of dilute solutions. It is then shown that for about thirty organic solvents, for which the

necessary data are available, $\eta_{25} \times \Lambda_{\infty}^{25} = \text{const.} = 0.7$, tetraethylammonium iodide being taken as solute throughout. The temperature coefficients, too, (1) of the fluidity, (2) of the conductivity, are practically equal in the case of each solvent. It is therefore to be expected that $\eta_0 \times \Lambda_{\infty}^0 = 0.7$, and this relationship is supported by the experimental data. These results may be summed up in the statement that when tetraethylammonium iodide is taken as solute with organic solvents the product of the viscosity and the conductivity at infinite dilution is independent of the temperature and of the nature of the solvent. It appears from the author's work that the mobility of the ions is determined not so much by the friction experienced by the ions themselves as by the friction of the particles of the solvent. This probably means that the moving ion is associated with a number of the molecules of the solvent, so that the friction it experiences is practically identical with that of the solvent itself. The number of associated solvent molecules will vary with the nature of the ion.

J. C. P.

Organic Solvent and Ionising Media. IV. Ebullioscopic Measurements. PAUL WALDEN (*Zeit. physikal. Chem.*, 1906, **55**, 281—302. Compare Abstr., 1904, ii, 227; this vol., ii, 149, 335).—The molecular condition of tetraethylammonium iodide, the substance chosen as a normal solute, has been studied by boiling-point measurements in the following solvents: methyl and ethyl alcohols, acetone, nitrile, propionitrile, nitromethane, and methyl thiocyanate. The boiling-point elevation constants of the last four solvents have been specially determined, and are found to be 13.0, 18.7, 19.5, and 26.4 respectively. As in the case of other solvents, these empirical constants are less (about 8 per cent.) than the values calculated from van't Hoff's expression, $0.02T^2/w$. When the values of i for tetraethylammonium iodide obtained from the ebullioscopic measurements are compared with those obtained from the conductivity measurements previously recorded, it is found that though they are of the same order there is by no means complete agreement. With the alcohols as solvents, the values of i obtained by the osmotic method are smaller than those obtained by the conductivity method, the divergence between the two sets of values increasing with the concentration of the solute. It appears that the greater the associating power of the solvent and the greater its mass relatively to that of the solute, the less marked is the tendency of the latter to associate and the closer is the approximation between the two sets of i values. With the nitriles and nitromethane as solvents, there is a satisfactory agreement between the two sets of i values. Addition of tetraethylammonium iodide to methyl thiocyanate actually lowers the boiling point of the latter, and an explanation of this anomalous behaviour has not yet been discovered.

J. C. P.

Diffusion of Hydrogen through Hot Platinum. ADOLF WINKELMANN (*Ann. Physik*, 1906, [iv], **19**, 1045—1055. Compare Abstr., 1902, ii, 552).—The experimental results obtained in earlier

work can be expressed equally well by the author's formula and by that of Richardson, Nicol, and Parnell (*Phil. Mag.*, 1904, [vi], 8, 1).

J. C. P.

Gaseous Osmosis through a Colloidal Membrane. JULES AMAR (*Compt. rend.*, 1906, 142, 779—781).—The permeability of a colloidal membrane to carbon dioxide was determined by weighing the amount of the gas which diffused through the membrane in thirty minutes on four consecutive days; the results were 20 mg., 16 mg., 12 mg., and 8 mg., showing that the osmosis diminishes as the membrane becomes dry, whilst if the membrane is perfectly dry the diffusion ceases entirely.

M. A. W.

Gaseous Osmosis through a Colloidal Membrane. JULES AMAR (*Compt. rend.*, 1906, 142, 872—874).—The author has shown that a perfectly dry animal membrane separating air and carbon dioxide both at atmospheric pressure is impermeable to the latter gas (compare preceding abstract). If the pressure of the carbon dioxide is gradually raised, osmosis begins when the pressure reaches a value corresponding with 12 to 14 mm. of petroleum, and the osmotic effect increases as the pressure is further increased. Under the increased pressure, it would seem that the carbon dioxide can dissolve in the membrane, and then only is the membrane permeable to the gas. After subjecting a dried colloidal membrane to a current of carbon dioxide under a pressure of 40 mm. of petroleum for twenty-four hours, it was found that about 30 mg. of carbon dioxide could be extracted by means of a mercury pump.

H. M. D.

Experimental Demonstration of Osmosis. ALFRED THIEL (*Zeit. Elektrochem.*, 1906, 12, 229—230).—When a drop of a cold saturated solution of potassium ferrocyanide is formed, by means of a pipette, under the surface of a solution of copper sulphate (0.5 molecule per litre), it first sinks to the bottom of the vessel. Owing to osmosis, it then swells and finally rises to the surface, the specific gravity of the solution of potassium ferrocyanide having become smaller than that of the copper sulphate owing to the passage of water through the copper ferrocyanide membrane.

T. E.

Nature of the Process of Osmosis and Osmotic Pressure with Observations concerning Dialysis. LOUIS KAHLBERG (*J. Physical Chem.*, 1906, 10, 141—209).—Considering the great importance of direct measurements of osmotic pressure for the van't Hoff theory of solutions, the number of such measurements is small, and much work has been done which indicates that the cause of osmotic phenomena is not to be found in the explanation due to van't Hoff (see Traube, *Abstr.*, 1905, ii, 13; Batelli, *ibid.*, ii, 629). The author's experiments were made in order to inquire into the nature of osmotic pressure and to test whether the latter really follows the gas laws. If ether be separated from chloroform by a layer of water, then, owing to the solubility of ether in water and its miscibility with chloroform, the ether passes through the aqueous layer into the chloroform.

Owing to the slight solubility of chloroform in water, the reverse flow is very limited. The water acts, therefore, as a semi-permeable septum. If cork saturated with water is employed, the existence of osmotic pressure may also be demonstrated. This illustrates the author's view of the nature of osmosis. If two liquids *A* and *B*, mutually soluble, be separated by a septum capable of absorbing *A*, then *A* passes through into *B*; the reverse flow also occurs to a slight extent, because the septum when saturated with *A* is then capable, to some extent, of dissolving *B*. This accords with the fact that no membrane is absolutely semi-permeable. It is, therefore, possible to predict the direction of the osmosis. Thus, india-rubber does not absorb water; it absorbs pyridine and alcohol, however, and these liquids pass through india-rubber into water. Acetic acid also passes through into water from a solution or from the pure acid. If a pyridine solution of silver nitrate is separated from water by an india-rubber septum, the pyridine passes through, but only traces of the silver salt which is not soluble in hydrocarbons, and hence not absorbed by the india-rubber. With parchment in place of india-rubber, the main flow is in the opposite direction, but some pyridine and silver nitrate pass into the water, a result which would be expected from the ready absorption of water by parchment. A very large number of experiments is recorded which are in complete accord with the author's views. Copper oleate is soluble in hydrocarbons and hence passes through india-rubber in benzene or pyridine solution; sugar, however, does not so pass, and it follows, therefore, that if a pyridine solution of both copper oleate and sucrose be separated from pure pyridine by a rubber membrane the non-crystalline or colloid substance passes through the septum. Similarly, camphor could be substituted for sucrose and two crystalline substances could be thus separated by dialysis. Quantitative measurements of the osmotic pressure were also made in cells with an india-rubber septum, and details of the construction of these cells are given. Pyridine was employed as the solvent, and sucrose, silver nitrate, and lithium chloride were the solutes. It was found that in order to obtain correct results for the pressure it is essential that the outer liquid and contents of the cell should be continuously stirred, and an ingenious contrivance for this purpose is described. It was found that the electrolyte, lithium chloride, gave lower pressures than the sucrose, and neither gave pressures at all approximating to those required by the gas laws. Further, the changes of pressure due to temperature changes are very much greater than they should be if proportional to the absolute temperature. The author considers it proved that the gas laws do not hold, and hence cannot serve as a basis for a satisfactory theory of solutions.

L. M. J.

Diffusion of Solutions and Molecular Weights. MICHEL YÉGOUNOW (*Compt. rend.*, 1906, 142, 954—957).—The author has determined the velocity with which a salt solution rises to a given height in a tube containing gelatin when the tube is partly immersed in the solution, and finds that the ratio of the coefficient of diffusion

(k) to the velocity (v) is constant for equal molecular solutions of all substances; for normal solutions, the value of the constant is 0.1.

M. A. W.

Methods of Deducing the Phase Rule. ALFRED BYK (*Zeit. physikal. Chem.*, 1906, 55, 250—256).—The author discusses the relative merits of Nernst's deduction of the phase rule, as given in his text-book, and the proof published by Wind (*Abstr.*, 1900, ii, 197). The advantages claimed for the latter are more apparent than real.

J. C. P.

Contributions to the Theory of Mixtures. JOHANNES D. VAN DER WAALS (*Arch. Néerland.*, 1906, [ii], 11, 115—148).—A mathematical paper.

J. C. P.

The Displacement of the Equilibrium of Univariant and of Bivariant Systems. PAUL SAUREL (*J. Physical Chem.*, 1906, 10, 108—118).—A mathematical paper in which the author applies the general equations of equilibrium displacement to the cases of univariant and bivariant systems of any number of components.

L. M. J.

Static Character of the Equilibrium of Physico-chemical Systems. A. GORBOFF (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 1216—1228).—The author discusses the equilibria of non-variant and univariant systems, and comes to the following conclusions. The equilibrium of physico-chemical systems is preserved in virtue of the conditions of experiment. It is not exhibited as a consequence of two opposite changes, since it is not probable that, at any appreciable surface of two co-existing phases, the mathematical equality of the two changes required by theory holds; consequently, it is realised as a result of a general law and in spite of chance. In a condition of equilibrium, the velocity of change is zero, so that equilibrium is not dynamic, but static, in character. Further, as regards the phenomenon of evaporation of homogeneous liquids, the kinetic hypothesis gives no explanation either of the capability of the liquid of separating, under the conditions of experiment, into two phases (liquid and vaporous), or of the constancy of the vapour pressure at constant temperature, or of the mechanical stability of a system consisting of a liquid and its saturated vapour.

T. H. P.

Studies in Chemical Affinity. I. J. N. BRÖNSTED (*Zeit. physikal. Chem.*, 1906, 55, 371—382).—The author calculates the affinity of a reaction, that is, the maximum of external work derivable from the change, for the case where there is a transition temperature, and where the manner in which the heat of the reaction varies with temperature is known. He arrives thermodynamically at the formula: $A = Q_0(T - T_0)/T_0 + (c_2 - c_1)[T \log_e T/T_0 - (T_1 - T_0)]$, where A is the affinity at the temperature T , Q_0 is the heat absorbed in the change at T_0 , the transition temperature, c_1 and c_2 are the specific heats of the initial and final systems respectively. The applicability

of this formula is tested for the allotropic change $S_{rh} \rightleftharpoons S_m$. A satisfactory agreement is found between the values of A calculated by the formula and those obtained from direct determinations of the affinity by means of solubility measurements. In the course of his work the author has found that the heat effect accompanying the change $S_{rh} \rightarrow S_m$ is 2.40 cal. per gram of sulphur. The molecular weight of sulphur in benzene and chloroform is that corresponding with the formula S_8 . The ratio s_m/s_{rh} , where s = solubility, is found to be 1.27—1.40 between 0° and 25.3° (values quite different from those found by Meyer, Abstr., 1903, ii, 137); the ratio of the solubilities is independent of the solvent used.

J. C. P.

Equilibria in Silver Chloride Solutions. ROGER C. WELLS (*J. Physical Chem.*, 1906, 10, 79—92).—The nephelometer described by the author and Richards (Abstr., 1904, ii, 287) affords a good method for determining the concentration of an ion in very dilute solution, and the author has used it to investigate the validity of the solution law in the case of solutions of silver chloride—that is, to determine the constancy of the product of the concentrations of the silver and chloride ions. In any given solution the silver was first precipitated by excess of chlorine ions, and in another portion the chlorine precipitated by excess of silver ions, and the method of using the nephelometer is slightly modified by the use of standard opalescent glasses, details being given. In the first series of experiments, the concentration of chlorine ions varied from 57 to 5 microequivalents (millionths) per litre, and the solubility product varied irregularly from 192 to 220. In another series, the concentration varied from 3 to 29, and the product varied from 98 to 111. The constancy is thus well established. The nephelometric observations were also completely verified by determinations of *E.M.F.* and the application of Nernst's formulæ.

L. M. J.

Esterification. RUDOLF WEGSCHEIDER [with ANTON KAILAN] (*Ber.*, 1906, 39, 1054—1057. Compare H. Goldschmidt and E. Sunde, this vol., ii, 219).—The esterification constant for benzoic acid gradually diminishes with the time when hydrogen chloride in absolute alcohol is used. This is not due to the hydrolysis of the ester formed, but to catalytic retardation by the water formed. When the alcohol contains small amounts of water, the constant does not fall to any appreciable extent with the time.

Direct proportionality between the constant and the concentration of the hydrogen chloride used as catalyst only holds for absolute alcohol; when appreciable amounts of water are present, the value K/c increases with c .

For any given concentration of the hydrogen chloride, the relationship between the velocity constant K and the concentration of the water W is expressed by the equation $1/K = \alpha + \beta W + \gamma W^2$. For $c = 0.858$ and W up to 1.15, $1/K = 20.47 + 28.17 W + 33.34 W^2$.

Errors may be introduced in preparing the hydrogen chloride solution unless rise of temperature, causing the formation of water, is avoided. The presence of small amounts of ethyl benzoate also affects the constant to a slight extent.

J. J. S.

Velocity of Formation of Oximes. PAVEL I. PETRENKO-KRITSCHENKO and W. KANTSCHIEFF (*Ber.*, 1906, **39**, 1452—1460. Compare Abstr., 1901, i, 505).—The rate of oxime formation has been determined in alcoholic solutions free from aldehyde. The unused hydroxylamine was titrated by Meyeringh's method. The following numbers give the percentage of compound transformed into oxime at the end of one hour: acetone, 82; methyl ethyl ketone, 79.2; methyl propyl ketone, 74.6; diethyl ketone, 37.9; ethyl propyl ketone, 36.8; dipropyl ketone, 31.4; methyl *n*-hexyl ketone, 67.6; methyl isopropyl ketone, 33.0; ethyl isopropyl ketone, 28.9; acetophenone, 9.2; benzaldehyde, 85.0; isobutaldehyde, 76.7; ketoheptamethylene, 44.2; ketohexamethylene, 92; ketopentamethylene, 61.8; propionyltetramethylene, 32.4; and acetyltrimethylene, 9.1. The results confirm those previously obtained for the reactivity of carbonyl compounds (Abstr., 1905, i, 354, 742).

The following values have been obtained for the esters of ketonic acids: $\text{Ac} \cdot \text{CO}_2\text{Et}$, 64.5; $\text{CH}_2\text{Ac} \cdot \text{CO}_2\text{Et}$, 51.5; $\text{CH}_2\text{Ac} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, 33.5; $\text{CHEtAc} \cdot \text{CO}_2\text{Et}$, 15.7; $\text{CAcEt}_2 \cdot \text{CO}_2\text{Et}$, 5.2; $\text{CO}(\text{CH}_2 \cdot \text{CO}_2\text{Et})_2$, 33.2; $\text{CO}(\text{CHMe} \cdot \text{CO}_2\text{Et})_2$, 9.6; $\text{CO}(\text{CHEt} \cdot \text{CO}_2\text{Et})_2$, 7.5;

$\text{O} \begin{array}{c} \text{CHMe} \cdot \text{CH}(\text{CO}_2\text{Et}) \\ \text{CHMe} \cdot \text{CH}(\text{CO}_2\text{Et}) \end{array} > \text{CO}$, 25.7; $\text{O} \begin{array}{c} \text{CHPh} \cdot \text{CH}_2 \\ \text{CHPh} \cdot \text{CH}_2 \end{array} > \text{CO}$, 69;

$\text{O} \begin{array}{c} \text{CHPh} \cdot \text{CH}(\text{CO}_2\text{Et}) \\ \text{CHPh} \cdot \text{CH}(\text{CO}_2\text{Et}) \end{array} > \text{CO}$, 15; $\text{NH} \begin{array}{c} \text{CHPh} \cdot \text{CH}(\text{CO}_2\text{Et}) \\ \text{CHPh} \cdot \text{CH}(\text{CO}_2\text{Et}) \end{array} > \text{CO}$,

4 per cent.

In these experiments, the excess of hydroxylamine was determined by titration with standard acid, using *p*-nitrophenol as indicator.

These numbers are discussed, and more especially the increased activity due to ring formation pointed out. J. J. S.

Critical Pressures of Solutions. MIECZYSLAW CENTNERSZWER and A. PAKALNEET (*Zeit. physikal. Chem.*, 1906, **55**, 303—314. Compare Centnerszwer, Abstr., 1904, ii, 158; Smits, *ibid.*, ii, 15).—The authors' experiments, made chiefly with solutions of triphenylmethane in ether, show that the critical pressure of a solution (meniscus in middle of tube) is greater than that of the pure solvent, and that the increase is proportional to the concentration of the solute. The critical part of the border curve for any given solution can be represented by the equation $\pi = \pi_0 + A(\theta - \theta_0)$, where π_0 and θ_0 are the critical pressure and temperature, π and θ are the corresponding quantities for the solution, and A is a constant independent of the concentration, and equal to the molecular increase of the critical pressure divided by the molecular rise of the critical temperature. In all the solutions, retrograde condensation of the first order has been observed both at constant temperature and at constant pressure. J. C. P.

Solubility Curves. JOSEPH E. TREVOR (*J. Physical Chem.*, 1906, **10**, 99—107).—A mathematical paper in which the author investigates the equations for the solubility in the case of a two-component system in a three-phase state. L. M. J.

Regularity in the Absorption of Gases by Liquids. LUDWIG W WINKLER (*Zeit. physikal. Chem.*, 1906, 55, 344—354. Compare Abstr., 1892, 556).—For a large numbers of gases and vapours dissolved in water, the author finds his earlier rule (*loc. cit.*) confirmed, the change in the absorption coefficient with the temperature being proportional to the change in the viscosity of the solvent. The numerical value of k (*loc. cit.*) varies with the number of atoms in the molecule of dissolved gas. Thus, the value of k for argon is about 4.4, the value for hydrogen, oxygen, and other diatomic gases is about 3.8, for triatomic gases about 3.2, and so on. The behaviour of helium is exceptional. For vapours which exhibit deviation from the condition characteristic of a perfect gas, k tends to increase with rising temperature.
J. C. P.

Solubility in Water of the Halogen Derivatives of Hydrocarbons. A. REX (*Zeit. physikal. Chem.*, 1906, 55, 355—370).—The author finds that at 20° 100 grams of water dissolve the following weights (in grams) of the substances named: methylene chloride, 2.0; chloroform, 0.822; carbon tetrachloride, 0.08; methylene bromide, 1.148; methyl iodide, 1.419; ethylene chloride, 0.869; ethylidene chloride, 0.550; ethyl bromide, 0.914; ethyl iodide, 0.403; propyl chloride, 0.272; isopropyl chloride, 0.305; propyl bromide, 0.245; isopropyl bromide, 0.318; propyl iodide, 0.107; isopropyl iodide, 0.140; carbon disulphide, 0.201.

The value of k in Winkler's formula (see preceding abstract), when calculated for each of a series of halogen derivatives containing a given number of atoms, is found to increase regularly with the molecular weight. The value of k for a given compound increases as the temperature rises (compare Winkler, *loc. cit.*).

In general, the author finds that the regularities observed by Winkler in the absorption of gases by water at various temperatures are to be found also in connection with the solubility of liquids in water. The conclusion is drawn that the solution of liquids in water is a process of absorption just as much as is the solution of gases.

J. C. P.

Mixed Crystals in Ternary Systems FRANS A. H. SCHREINEMAKERS (*Arch. Néerland.*, 1906, [ii], 11, 53—114).—A résumé of work published previously (Abstr., 1905, ii, 154, 376, 685).
J. C. P.

Formation of Solid Surfaces in Solutions of Dyes: Photoelectric Effects in the Case of these and of Metallic Sulphides. OTTO RÖHDE (*Ann. Physik*, 1906, [iv], 19, 935—959).—Observation of aqueous solutions of magenta and methyl-violet shows that the surface of the liquid gradually becomes more concentrated, then tough, and finally rigid and brittle, the solution being then covered with a skin of the solid dye. The molecular forces which cause this separation of the solid dye are probably the same as those which are active in the phenomena of surface tension. The more concentrated the solution the thicker is the skin which is formed, and the more rapid is its formation. Aqueous solutions of magenta and methyl-violet exhibit marked photoelectric effects, due entirely to the skin already described.

A number of metallic sulphides have been examined and are all found to exhibit photoelectric effects. These are independent of the way in which the sulphide has been prepared, and are conditioned chiefly by the character of the surface, the density, and the molecular structure (crystalline form, for example). J. C. P.

Condition of the Colouring Matter in Artificially Coloured Crystals. P. GAUBERT (*Compt. rend.*, 1906, 142, 936—938. Compare this vol., ii, 152).—If the coloured crystals are only formed in solutions nearly saturated with the colouring matter, they have the same colour as the crystals of the colouring matter, and the directions of maximum and minimum absorption are not in any way related to the axes of the crystal. If, on the other hand, the coloured crystals are formed independently of the concentration of the colouring matter in solution, the colour may be different from that of the crystals of the colouring matter, but the directions of maximum and minimum absorption are determined by the axes of the crystal.

The author has crystallised phthalic acid from aqueous solutions containing methylene-blue, and found that the colouring matter distributes itself in a constant ratio between the crystals and the solution, indicating that the molecular condition is the same in the solid as in the liquid solution. Crystallisation of coloured solutions of carbamide nitrate gave similar results. H. M. D.

The Transition from Crystalline to Colloid Substances. BASIL B. KURILOFF (*Zeit. Elektrochem.*, 1906, 12, 209—218).—The precipitation of solutions of zinc chloride by ammonia is studied. When the quantity of ammonia added is less than one molecule to one equivalent of zinc, the precipitate consists of the basic salt, $\text{ZnCl}\cdot\text{OH}\cdot\text{Zn}(\text{OH})_2$, and the equilibrium reached is in agreement with the laws of the action of mass.

With larger quantities of ammonia, the composition of the precipitate undergoes a gradual change, chlorine being eliminated and ammonia absorbed. The precipitate finally dissolves entirely to a colloidal solution of zinc hydroxide. This solution is precipitated by dilution. The laws of mass action do not apply to the equilibria in which the colloidal zinc hydroxide occurs, and its composition cannot be represented by any ordinary chemical formula. T. E.

Amorphous Precipitations. I. Partial Cleavage of Bivalent Bases on Precipitation of Chromic or Aluminium Hydroxide. DANIEL STRÖMHOLM (*Arkiv. Kem. Min. Geol.*, 1906, 2, No. 9, 1—13).—Starting from the law of mass action, the author proceeds to determine the criteria for a precipitate consisting of a chemical compound or of an adsorption, examples being taken from the actions of bivalent bases on chromic and aluminium hydroxides. In the first case, the composition of the precipitate or the concentration of the non-dissociated hydroxide in the solution must be constant. If, however, there exists only a solid phase with varying composition, the concentration of the bivalent hydroxide in the precipitate raised to a certain

power (α) must stand in a constant ratio to the concentration of the same hydroxide in the solution.

Solutions of aluminium (or chromium) chloride, ammonium chloride, calcium (or magnesium or barium) chloride, and ammonia of various concentrations were mixed and analysed after the lapse of different intervals of time, the composition of the precipitate being thereby determined. The results, which are given in detail, are briefly as follows. The violet chromic hydroxide dissolves magnesium hydroxide far more readily than does the green variety. If magnesium sulphate is employed in place of the chloride, a green chromic hydroxide separates, which exhibits a diminished solvent power for magnesia, but with aluminium hydroxide no such difference is observed. In none of the cases examined is a chemical compound between the ter- and bivalent hydroxides found to exist, only adsorptions being formed. The value of α in any one series of experiments is moderately constant, and is generally 3, less often 5—6. T. H. P.

Amorphous Precipitations. II. Basic Salts of Bivalent Metallic Oxides. DANIEL STRÖMHOLM (*Arkiv. Kem. Min. Geol.*, 1906, 2, No. 16, 1—13. Compare preceding abstract).—The author mixed solutions of the salts of lead, copper, zinc, or nickel with solutions containing sodium carbonate, sodium hydrogen carbonate, and sodium hydroxide in varying proportions, and analysed the solution after equilibrium had been attained. In solutions containing much carbon dioxide, a certain amount of copper, nickel, and zinc remains dissolved. The compositions of precipitate and solution do not vary continuously, but exhibit no distinct sudden changes such as would indicate the formation of chemical compounds.

In the case of lead, basic carbonates, $5\text{PbO}, 3\text{CO}_2$ and $3\text{PbO}, 2\text{CO}_2$, are formed. In solutions containing but little carbon dioxide, lead hydroxide quite free from carbon dioxide is obtained, whilst if much carbon dioxide is present, pure lead carbonate is formed; with intermediate proportions of carbon dioxide, the solutions deposit mixtures of the hydroxide and carbonate. With copper, no salts having definite formulæ were detected. In the case of zinc, a salt of the composition $5\text{ZnO}, 2\text{CO}_2$ is found to exist in equilibrium with solutions containing varying proportions of carbon dioxide. With nickel, the colour of the precipitate changes greatly with its content of carbon dioxide; the existence of $3\text{NiO}, \text{CO}_2$ is probable.

The formation of definite basic carbonates renders probable the existence of basic salts of stronger acids. It is shown that the following salts are formed as definite chemical individuals: $4\text{CuO}, \text{SO}_3$; $4\text{CuO}, \text{N}_2\text{O}_5$; $4\text{ZnO}, \text{SO}_3$; $6\text{NiO}, \text{SO}_3$; $6\text{CoO}, \text{SO}_3$. T. H. P.

Adsorption Phenomena, with Special Reference to the Action of Electrolytes and the Ash-constituents of Proteids. WILLIAM M. BAYLISS (*Bio-chem. J.*, 1906, 1, 175—232).—Adsorption is something intermediate between chemical combination and mechanical admixture. Ostwald has pointed out that there is no hard and fast distinction between it and chemical union, and speaks of “mechanical

affinity" in relation to it. The laws of adsorption discovered by previous workers in reference mainly to dyes show that the dye is taken up in relatively larger quantities the more dilute the solution. If a curve is constructed in which the ordinates represent the percentage of dye left in solution, and the abscissæ the original concentration, it is found, in confirmation of Ostwald, to be a hyperbola. This curve only approaches the axis (that is, zero concentration) asymptotically. It follows, therefore, that in order to wash out the dye by a solvent, an infinite number of successive washings is necessary.

Exactly the same laws hold for the ash-constituents, which it is so difficult to remove from proteids. The case of gelatin is specially considered; the curve of electrical conductivity of successive distilled water extracts of gelatin is a hyperbola; it is therefore impossible to wash out all the electrolytes except by an infinite number of changes of distilled water, each change removing a less percentage than the previous one; in other words, they are present in an adsorbed form.

When the gelatin is washed nearly free from such admixtures, and is placed in solutions of electrolytes, it again adsorbs them in a non-ionised condition, and so the conductivity of the solution is diminished.

The rate at which Congo-red is taken up by paper is accelerated by rise of temperature, but the total amount taken up when equilibrium is reached is less the higher the temperature; the temperature-coefficient of the reaction velocity is very low, so that Nernst's theory as to the part taken by diffusion in heterogeneous reactions seems to apply to adsorption. At low temperatures, equilibrium is attained slowly; at room temperature, twenty-four hours are necessary. The adsorption compound of gelatin and inorganic electrolytes is also dissociated as the temperature rises, and no evidence of heat production in adsorption is obtained. The reaction between Congo-red and paper is reversible, so also is that between gelatin and electrolytes. It is, however, noticed, that raising the temperature rapidly to 100° tends to fix Congo-red in paper.

Dyes forming colloidal solutions are extremely sensitive to electrolytes in regard to their adsorption, the effect being proportional to the size of the colloid particles; in the case of electro-negative dyes (Congo-red), cations facilitate adsorption, anions depress it; with electro-positive dyes (toluidine-blue), the opposite is seen, but in both cases the effect of anions is small. Bivalent cations have much more than twice the effect of univalent ones.

Salts of the heavy metals which form positively-charged colloidal hydroxides powerfully promote adsorption of Congo-red. The facilitating ion is carried down with the dye. The presence of a stable colloid such as gelatin protects Congo-red from the action of electrolytes. A negative charge seems necessary for this action, since egg-albumin exercises the same effect in alkaline solution, and the opposite effect in acid solution. The explanation of the action of electrolytes, as well as that of other electrically-charged colloids, is to be found in the negative charge of non-conductors like paper when immersed in water (Quincke). The different behaviour of silk and paper towards electro-positive and -negative dyes, as also the influence of alcohol on the process, is to be explained by the results obtained by Cöhn on the

influence of the respective dielectric constants on the charge. When gelatin is precipitated by tannin, its adsorbed electrolytes are split off.

There is no evidence of a sudden separation of electrolytes in the tissues at the moment of death, but there is a gradual one when a living tissue is warmed from 11° to 56°. In the process of blood-clotting, there is a diminution of electrical conductivity, ions (probably of calcium) disappearing from solution. In the action of rennet on milk, there is a slight increase in conductivity, an additional fact showing this process to be quite different from blood-clotting. In all probability, rennet action is only an expression of pepsin action in neutral or faintly alkaline medium (Pawloff). A further paper is, however, promised on the application of these facts to enzyme action.

Many applications of the subject are pointed out in relation, for instance, to the action of soils, the purification of sewage, and the theory of dyeing; the theory proposed in relation to dyeing is very like that reached by Picton and Linder by different methods. In the staining of histological preparations, the evidence is in favour of the adsorption theory; cases of true chemical combination are rare; the part played by electrolytes must also be taken into account. If electrolytes are split off from living cells on death or injury, it is clear why such cells readily take up acid dyes; moreover, since electrolytes are unnecessary when the substance to be stained is electro-negative, it is clear why living cells can be stained with basic dyes. Macdonald's results with neutral-red and injured nerve fibres are difficult to explain by such a theory: evidently here other factors have to be considered. The affinity of Nissl's granules for basic dyes is abolished by previous treatment with neutral salts (Mayer); this is in accordance with the present results.

Evidence is adduced that the action between toxins and anti-toxins is adsorptive, and that the union between an enzyme and colloidal substance is of the same nature; the adsorption of trypsin by paper is facilitated by calcium sulphate.

The nature of the compounds between acid and basic dyes was also investigated. They appear to be uncharged colloids, but the evidence as to whether they are colloidal adsorption compounds or true chemical compounds is not decisive.

W. D. H.

Capacity of the Elements for entering into Chemical Combination. GUSTAV TAMMANN (*Zeit. anorg. Chem.*, 1906, 49, 113—121).—In the present paper, only the formation of binary crystalline compounds between the reacting elements is taken into account. The data are taken from papers by Roozeboom, Heycock and Neville, Le Chatelier, the author, and others.

It is shown that, excluding the two short periods of Mendeléeff's table, the immediately consecutive elements of a natural group in the more restricted sense (such groups usually consisting of three elements, for example, copper, silver, gold) do not enter into chemical combination; the only well-proved exception to this rule is the existence of the compound BrI (Terwogt, this vol., ii, 15). The analogous elements in the two short periods, such as oxygen and sulphur, carbon and silicon, form well-defined compounds, so that the rule only holds for those elements

occupying central positions in the periodic table, but is not true of those near the margins.

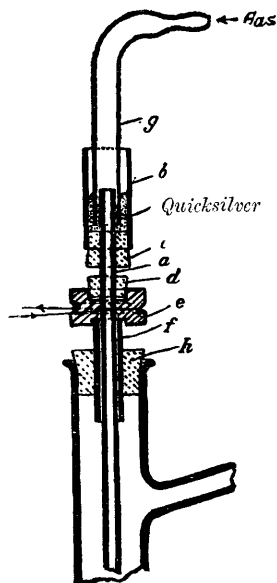
Further, when the combining capacity of any one element towards the members of a natural group is considered, it is found that, in general, either all or none of the members of the group combine with the element in question. The applicability of this rule, to which there are a good many exceptions, is fully discussed in the paper.

In conclusion, it is pointed out that these rules correspond to some extent with a regularity discovered by Kayser and Runge, according to which the spectra of the elements of a natural group, in the more restricted sense, possess an analogous constitution. G. S.

Production of High Vacua by means of Liquid Air. GEORGES CLAUDE and RENÉ J. LÉVY (*Compt. rend.*, 1906, 142, 876—877).—An apparatus is described for rapidly attaining high degrees of exhaustion by a series of steps, in each of which the receiver is put in connection with fresh charcoal cooled in liquid air. The cooling tubes are put in or out of circuit by means of mercury columns worked by pistons, and in order to eliminate the influence of mercury vapour, the parts of the apparatus immediately above the mercury columns are cooled by liquid air.

H. M. D.

Simple Arrangement for Passing Gases into Reacting Masses which are stirred by a Turbine. K. BURKHEISER and G. CHRISTIE (*Chem. Centr.*, 1906, i, 1073; from *Zeit. chem. Apparatenkunde*, 1, 158).—The glass tube, *a* (7—8 mm.), which forms the stirrer, is securely fastened to the driving pulley, *e*, by means of a rubber bung, and the pulley rests on the wide glass tube, *f*. The bung, *e*, which closes the lower end of the tube *b*, is fitted tightly on to the stirrer, *a*, which projects through the bung as shown in the sketch. The joint between the gas delivery tube, *g*, and the stirrer is made by pouring mercury into *b* to the depth of 2 cm. A second hole in the bung, *h*, allows the gas to escape. If the gas requires to be delivered under greater pressure the tubes are suitably lengthened, so that a deeper mercury lute may be used, and if the contents of the flask are to be heated a Schwickerath flask is employed. When solids are formed by the action of the gas, the motion of the stirrer projects them to the sides of the vessel, and thus prevents the choking of the tube.



E. W. W.

Inorganic Chemistry.

Hydrogen Chloride Generating Apparatus. FRIEDRICH W. KÜSTER and FRITZ ABEGG (*Chem. Centr.*, 1906, 885—886; from *Zeit. chem. Apparatenkunde*, 1, 89—93).—The apparatus consists essentially of a 3—4 litre bottle, which is about half filled with crude concentrated sulphuric acid, and is connected by means of a vertical tube fitted with a stopcock and screw clamp with an upper vessel containing crude concentrated hydrochloric acid. The flow of the hydrochloric acid is regulated by the clamp, and the quantity passing into the lower vessel may be seen by means of the sight tube which is fitted below the clamp; this tube consists of a narrow tube or jet fused into a bulb. The bottle which contains the sulphuric acid is fitted with an emptying cock and a safety tube connected with a reservoir. When the flow of acid is stopped, the pressure caused by the small quantity of gas which is subsequently liberated is relieved by means of the safety tube or by opening a cock in a T-piece which is attached to the delivery tube.

E. W. W.

Electrolytic Formation of Thiosulphates. MARIO G. LEVI and MARIO VOGHERA (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 322—328. Compare this vol., ii, 81).—The authors have made experiments to see if oxidation occurs in the electrolytic formation of thiosulphates (*loc. cit.*). They find no trace of tetrathionate, the formation of which is prevented by the high potential difference at the electrodes and by the agitation of the anodic liquid by the hydrogen. Using anodes of platinised platinum, the yield of thiosulphate is 24·8 per cent., whilst with nickel it is only 4·6, with lead 9·9, with peroxidised lead 6·4, and with iron 4·6 per cent.; in some cases sulphur is separated, and in others sulphides are formed. Increase of the alkalinity by addition of sodium hydroxide is accompanied by a large diminution in the yield, the S²⁻ ion reacting with the sodium hydroxide. The greatest yield is obtained when the solution contains only a little sodium carbonate.

T. H. P.

Sensitiveness of Selenium to Light. NICOLAUS A. HESEHUS (*Chem. Centr.*, 1906, i, 1080—1081; from *Physikal. Zeit.*, 7, 163—169).—A simple method of distinguishing soft from hard selenium is described in the original paper. Strong light temporarily affects both kinds of selenium. The time required for the element to regain its original condition depends simply on the duration of the exposure to light, but shaking has a great influence on the recovery. The effect of light is due to the selenium itself and not to selenides, the phenomenon being caused by an allotropic dissociation. When selenium is exposed to light of great intensity, the dissociation is increased owing to the penetration of the light to a greater depth.

E. W. W.

Nitrosylselenic Acid. VICTOR LENHER and J. H. MATHEWS (*J. Amer. Chem. Soc.*, 1906, **28**, 516—518).—By the action of liquid nitrogen tetroxide on concentrated selenic acid cooled with solid carbon dioxide, the compound, $\text{SeO}_2(\text{O}\cdot\text{NO})_2$, is obtained as a dark blue solid which melts at -13° and decomposes above this temperature into the nitrogen oxide and selenic acid. Nitrosylselenic acid, $\text{OH}\cdot\text{SeO}_2\cdot\text{O}\cdot\text{NO}$, could not be obtained. E. G.

Some Properties of Liquid Nitrogen. HUGO ERDMANN (*Ber.*, 1906, **39**, 1207—1211. Compare Abstr., 1905, ii, 81; Erdmann and Bedford, Abstr., 1904, ii, 328, 557).—An apparatus is described for condensing large quantities of nitrogen, which can now be obtained commercially containing only small amounts of impurities. Liquid nitrogen can be filtered rapidly through a folded filter, and is then a clear, mobile, colourless liquid, which has a sp. gr. lower than that of ice or solidified alcohol. Anhydrous oxygen under the ordinary pressure condenses when cooled by liquid nitrogen, but not by liquid air. Liquid ozone dissolves slowly in liquid nitrogen, forming a clear blue solution.

A table is given of the coefficients of expansion of oxygen and nitrogen at varying temperatures and under varying pressures; the coefficient of oxygen varies from 0.004291 for the temperature interval 11 — 132° under 1.4 mm. pressure to 0.003668 at 100° under 759 mm. pressure, whilst that of nitrogen varies from 0.002996 for the temperature interval 11 — 132° under 0.6 mm. pressure to 0.003674 at 100° under 1000 mm. pressure. G. Y.

Atomic Weight of Nitrogen. PHILIPPE A. GUYE (*Ber.*, 1906, **39**, 1470—1476. Compare Gray, Trans., 1905, **87**, 1601; Guye, Abstr., 1904, ii, 475, 557, 812; 1905, ii, 442, 506, 702; this vol., ii, 20).—The values for the atomic weight of nitrogen determined by physico-chemical methods vary between 14.006 and 14.012 with a mean of 14.008. The values are obtained from density determinations of nitrogen, ammonia, nitrous oxide, and nitric oxide, and allowances have been made for deviations from Avogadro's law. The values obtained by chemical methods, namely, by analysis of nitrous and nitric oxides, vary between 14.002 and 14.015 with a mean of 14.010. The mean of the two values, namely, 14.009 or 14.01, is regarded as the correct atomic weight of nitrogen. J. J. S.

Oxidation of Ammonia. OTTO SCHMIDT and RUDOLF BÖCKER (*Ber.*, 1906, **39**, 1366—1370).—When a mixture of ammonia and air or oxygen is heated in the presence of platinum or platinised asbestos at a low red heat, a 75 per cent. yield of oxides of nitrogen is obtained. The initial product is nitric oxide, which subsequently is converted mainly into nitrogen trioxide. C. S.

Theory of Ammoniacal Compounds. BASIL KURILOFF (*Ann. Chim. Phys.*, 1906, [viii], **7**, 568—574).—The author regards the ammoniacal compounds of metallic salts as divisible into three classes. There are, first, ammoniacal compounds of constant composition, in

which the relative proportion of ammonia and metallic salt is a simple one; second, ammoniacal compounds the composition of which is not constant, but in which a variable number of molecules of ammonia may be combined with one molecule of a salt (compare *Bull. Acad. St. Petersb.*, 1902, 17, and Reychler, *Abstr.*, 1904, ii, 403); and third, a colloidal class in which there is no definite relationship between the quantities of ammonia and metallic salt present.

The author's investigation of the action of ammonia on zinc chloride shows that compounds of the first class may pass readily into those of the second or third class. The second type of ammoniacal compound is analogous in properties with hydrates, molecular compounds, complex silicates, and similar substances (compare van Bemmelen, *Abstr.*, 1904, ii, 18), whilst the third is similar in character to the hydrogels (compare Duclaux, *Abstr.*, 1904, ii, 162, 243, 325, and van Bemmelen, *Abstr.*, 1897, ii, 137; 1899, ii, 12, 84; 1902, ii, 70; 1904, ii, 18).

T. A. H.

Action of Hydrogen Peroxide on Phosphorus. THEODOR WEYL (*Ber.*, 1906, 39, 1307—1314).—Hydrogen phosphide is evolved when yellow phosphorus is warmed with water. A 6 per cent. aqueous solution of hydrogen peroxide acts on yellow phosphorus at about 60°; a 30 per cent. solution behaves similarly, phosphorus and phosphoric acids being also formed. The action of hydrogen peroxide on amorphous phosphorus or on Schenck's phosphorus is much more energetic than is its action on yellow phosphorus, the action being violent with solutions which contain more than 8 per cent. of the peroxide; the products are in this case also hydrogen phosphide, phosphorous acid, and phosphoric acid. Hydrogen phosphide is evolved when amorphous phosphorus is boiled with water; the action is not due to any alkali derived from the glass vessels used.

The evolution of hydrogen phosphide from amorphous phosphorus or from Schenck's phosphorus by the action of boiling water, sodium hydroxide, or hydrogen peroxide is not to be ascribed to the presence of yellow phosphorus.

A. McK.

Variations in certain Properties of Quartz. HENRI BUISSON (*Compt. rend.*, 1906, 142, 881—883).—The density, coefficient of expansion, indices of refraction, and rotatory power of two apparently perfect cubes of quartz, one of 4 cm., the other of 5 cm., edge, have been accurately measured. The numbers obtained are all very slightly smaller for the larger cube. The properties of well-crystallised quartz appear to vary therefore to a measurable extent.

H. M. D.

Influence of Viscosity in Silicate-fusions. CORNELIUS DOELTER (*Centr. Min.*, 1906, 193—198. Compare *Ann. Rep.*, 1904, 1, 227; 1905, 2, 269).—Viscosity has an important influence on the behaviour of silicate-fusions; the greater it is, the less are the rates of solution, crystallisation, fusion, diffusion, &c.; eutectic mixtures are less likely to be formed, and the fusion may more readily become supersaturated and supercooled, and so consolidate as a glass. The rock-forming silicates

(felspars, pyroxenes, &c.) are much more viscous than the minerals of slags (melilite, åkermanite, fayalite, rhodonite, &c.), and still more so than alloys; the results obtained from the latter cannot therefore be applied to the former.

L. J. S.

Colloidal Sodium Chloride. CARL PAAL (*Ber.*, 1906, 39, 1436—1441).—The additive compounds of ethyl chloroacetate with ethyl sodiomalonate and similar substances (Michael, *Abstr.*, 1905, i, 855) show unexpected stability; hence the author concludes that the reaction proceeds in the normal way and the sodium chloride remains as an *organosol* in the benzene. If an excess (5—6 vols.) of light petroleum of low boiling point is added to the orange-coloured, opalescent benzene solution of the reaction-product of ethyl chloroacetate and ethyl sodiomalonate, a white, flocculent precipitate containing 65—70 per cent. of sodium chloride is obtained, and the filtrate is free from salt. This behaviour is not due to the decomposition of an additive compound, because other anhydrous solvents, excepting methyl and ethyl alcohols, do not cause precipitation; moreover, the freshly-precipitated substance retains its *sol* character, dissolving in benzene to an orange-coloured, opalescent solution, from which it is reprecipitated unchanged by light petroleum. The precipitate is not the pure sodium chloride *organosol*, but an adsorption compound of this and an organic complex.

Attempts to separate the colloidal sodium chloride by dialysis cause the formation of the *gel* containing 80 per cent. of sodium chloride. The *gel* obtained by drying the *sol* is an orange-coloured, amorphous substance which dissolves completely in water forming a solution neutral to litmus.

C. S.

Colloidal Sodium Chloride. FRITZ EPHRAIM (*Ber.*, 1906, 39, 1705).—A claim for priority (compare *Abstr.*, 1902, i, 269; Paal, preceding abstract).

C. S.

Two Acid Sodium Sulphates. JOH. D'ANS (*Ber.*, 1906, 39, 1534—1535).—The author confirms the existence of trisodium hydrogen sulphate, $\text{Na}_3\text{H}(\text{SO}_4)_2$, which crystallises in glistening needles, when a molecular solution of sodium sulphate and sulphuric acid is concentrated and cooled. The hydrate, $\text{Na}_3\text{H}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, is formed when sodium sulphate and sulphuric acid in the proportion to form trisodium hydrogen sulphate are added to a hot solution containing 16.5 per cent. of sulphuric acid and 35 per cent. of sodium sulphate; the resulting solution remains often persistently supersaturated, but on addition of a small crystal the hydrate separates in glistening, rhombic prisms, which weather slowly on exposure to air.

The solubility of sodium sulphate in dilute sulphuric acid rises rapidly with the strength of the sulphuric acid until with 8.67 per cent. of sulphuric acid the saturated solution contains 32 per cent. of sodium sulphate; from this point onwards, the solubility increases only slowly, rising to 33.6 per cent. of sodium sulphate in 15.4 per cent. sulphuric acid; after which the solubility slowly decreases with each further increase in the percentage of sulphuric acid.

The metastable solution containing 16.35 per cent. of sulphuric acid and 34.6 per cent. of sodium sulphate is saturated to both sodium sulphate and trisodium hydrogen sulphate. G. Y.

Commercial Preparation of Calcium Hydride. GEORGE F. JAUBERT (*Compt. rend.*, 1906, 142, 788—789. Compare Moissan, *Abstr.*, 1899, ii, 25).—Calcium prepared at the rate of 100 kilograms per hour by electrolysis of the fused chloride with a current of 7500 amperes and 20 volts is heated in a current of hydrogen in horizontal retorts. The crude calcium hydride thus obtained contains 90 per cent. of the pure compound mixed with the oxide and nitride, and is employed in aeronautics, for on decomposition with water it yields 1 cubic metre of hydrogen per kilogram, which is equivalent to a lifting power of 1200 grams. M. A. W.

Earth Alkali and Allied Peroxides: Properties and Applications. R. VON FOREGGER and HERBERT PHILIPP (*J. Soc. Chem. Ind.*, 1906, 25, 298—302).—Commercial calcium peroxide which has no water of crystallisation is a compound of calcium peroxide with calcium hydroxide and contains about 60 per cent. of the peroxide; its average sp. gr. is 0.603. It yields a larger percentage of available oxygen than the crystalline hydrate of the formula $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$, into which it can be converted. A third variety having the composition $\text{CaO}_2 \cdot 2\text{H}_2\text{O}$ is also known; when the commercial variety is added to water, it forms this substance and then undergoes a molecular change as shown by the equation $\text{CaO}_2 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}_2$. The complete decomposition of calcium peroxide in aqueous solution is only effected after boiling for several hours; in a dry atmosphere it may be heated to 200° without decomposing, and it is non-explosive. It stands midway between neutral and acid solutions of calcium permanganate in the amount of available oxygen which it can produce, but has the advantage over these of yielding insoluble calcium sulphate as the only by-product.

Commercial strontium peroxide is also dehydrated and consists of 85 per cent. of peroxide with 15 per cent. of hydroxide. It has a sp. gr. 0.546. Like calcium peroxide, it is very stable in a dry atmosphere, and can be heated to 150° without loss in available oxygen; it is partially decomposed by water without the aid of acids.

Commercial magnesium peroxide consists of peroxide and hydroxide and water; it ordinarily contains 8 per cent. of available oxygen, and has a sp. gr. 0.615; it can be heated in a dry atmosphere to 160° without decomposition.

Commercial zinc peroxide is a yellowish-white powder of sp. gr. 1.571 containing 50 per cent. of peroxide, the remainder being hydroxide and moisture. It does not lose its oxygen when heated in dry air to 170°. P. H.

Solubility of Gypsum in Solutions of Ammonium Sulphate. JAMES M. BELL and W. C. TABER (*J. Physical Chem.*, 1906, 10, 119—122).—The experiments of Cohn and of Sullivan prove that the solubility of gypsum decreases with increasing ammonium sulphate, but after-

wards increases. Neither observer obtained a double sulphate of calcium and ammonium, and it is possible therefore that such double sulphate, stated by Fassbender to be formed at 40—50°, is not stable at the temperature of Sullivan's experiments (25°). The author has therefore investigated the solubility curve for the system calcium sulphate, ammonium sulphate, water at the temperature 50°. The results indicate a short decrease in solubility of the gypsum, which afterwards increases to a maximum at about 420 grams per litre of ammonium sulphate; at this point the composition of the solid phase changes, the double salt, $\text{CaSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, being formed, the solubility of which decreases to about 560 grams of ammonium sulphate, after which the latter salt forms the solid phase. The composition of the double salt was determined by finding the composition of the solid which could be added to the solution without changing its composition (see Abstr., 1902, ii, 495). L. M. J.

Solubility of Gypsum in Magnesium Sulphate Solutions. FRANK K. CAMERON and JAMES M. BELL (*J. Physical Chem.*, 1906, 10, 210—215).—Owing to the difficulty of determining small quantities of calcium in the presence of large quantities of magnesium salts, the weight of gypsum dissolved was found from the loss of weight of a crystal of selenite. The solubility curve found is remarkable, exhibiting a minimum and maximum; the solubility falls from 2.046 (grams per litre) to about 1.46 at 13 grams per litre of MgSO_4 . It then increases to a maximum of about 1.64 at 105 grams MgSO_4 , after which it decreases to 0.5 in a saturated solution of magnesium sulphate. The temperature throughout was 25°. The author suggests that the peculiar form of the curve may be due to (1) changes in density of the solvent or (2) opposing influences of sulphion and magnesium (see Abstr., 1904, ii, 544; 1905, ii, 388). L. M. J.

Relative Solubility of Certain Sparingly Soluble Calcium and Barium Salts. HARRY W. FOOTE and GEORGE A. MENGE (*Amer. Chem. J.*, 1906, 35, 432—445).—Experiments have been carried out with the object of determining the relative solubility of calcium and barium carbonates, oxalates, and fluorides in water at the ordinary temperature. The sparingly soluble calcium salt was treated with a solution of barium chloride of known strength, and the corresponding barium salt with an equivalent solution of calcium chloride. The mixtures were shaken until equilibrium was established, and the proportions of barium and calcium in the solution were then estimated. The results are tabulated.

It is shown from theoretical considerations that the relative solubility of the salts is expressed by the square root of the ratio of the calcium and barium chlorides on the assumption that the sparingly soluble salts do not undergo hydrolysis, or by the cube root of this ratio, assuming that the pure salts hydrolyse completely. In the case of the carbonates, the relative solubility $\text{CaCO}_3/\text{BaCO}_3$ is 1.31 calculating on the former assumption, or 1.20 calculating on the latter assumption. It was found that a certain proportion of mixed crystals

was formed in the experiment, and on making a correction for this the relative solubility becomes 1.15. In the case of the oxalates, the relative solubility $\text{CaC}_2\text{O}_4/\text{BaC}_2\text{O}_4$, assuming that no hydrolysis occurs, was found to be 0.22. The results obtained with calcium and barium fluorides were only of qualitative interest and showed that barium fluoride is very much more soluble than the calcium salt.

The relative solubilities of the carbonates and oxalates obtained by this method are compared with those calculated from the absolute solubilities of these salts as determined by Kohlrausch and Rose (Abstr., 1894, ii, 7), and are found to be in fair agreement. E. G.

Dissociation of Barium Carbonate. ALEXIS FINKELSTEIN (*Ber.*, 1906, 39, 1585—1592. Compare Isambert, Abstr., 1878, 373; Brill, Abstr., 1905, ii, 522).—The author has investigated the dissociation of barium carbonate by Isambert's method (*loc. cit.*). After being dried at 1000° in a current of carbon dioxide, barium carbonate was heated in a platinum boat (which is not attacked in the absence of oxygen) in a glazed porcelain tube in a current of nitrogen. The tube was heated below 1200° by means of a Heraeus platinum spiral, above 1200° by a carbon resistance. The temperatures were measured by a Le Chatelier thermo-element. The current of nitrogen was passed at the rate of 1 litre in thirty minutes, and the carbon dioxide in the issuing gas determined. At high temperatures, the nitrogen was mixed with an amount of carbon dioxide less than that corresponding with the partial pressure at the given temperature. At temperatures between 915° and 1100° , the partial pressures of the barium carbonate as observed agree well with those calculated by the equation: $\log p_1/p_2 = 1.43 \times 10^4 (T_1 - T_2)/(T_1 T_2)$. From 1100° to 1350° , the partial pressures as observed were lower than the calculated. The temperature of decomposition of barium carbonate under 750 mm. pressure is found by extrapolation to be 1352° . This would not be observed experimentally, because of the fusion of the surface of the carbonate. Undissociated barium carbonate does not melt at 1350° , but the basic carbonate melts below 950° (compare Le Chatelier, Abstr., 1887, 431).

The basic carbonate, $\text{BaO}, \text{BaCO}_3$, is formed by prolonged heating of the carbonate at 1120° , and dissolves barium oxide, as also, at higher temperatures, barium carbonate. The partial pressures of the basic carbonate observed between 1020° and 1250° agree with those calculated by the equation: $\log p_1/p_2 = 1.335 \times 10^4 (T_1 - T_2)/(T_1 T_2)$. The temperature of decomposition of the basic carbonate under 750 mm. pressure is found by extrapolation to be 1454° (compare Brill, *loc. cit.*). In carbon dioxide under pressures higher than the corresponding pressure of barium carbonate at the given temperature, the basic carbonate is converted, but not completely, into the carbonate; when treated with water, it forms barium hydroxide and barium carbonate.

The heats of reaction are expressed by the equations: (1) $2\text{BaCO}_3 = \text{BaO}, \text{BaCO}_3 + \text{CO}_2 - 6.53 \times 10^4$ cal. (2) $\text{BaO}, \text{BaCO}_3 = 2\text{BaO} + \text{CO}_2 - 6.11 \times 10^4$ cal. (3) $\text{BaCO}_3 + \text{BaO} = \text{BaO}, \text{BaCO}_3 - 0.21 \times 10^4$ cal. (4) $\text{BaCO}_3 = \text{BaO} + \text{CO}_2 - 6.32 \times 10^4$ cal. It follows that the specific heat of barium carbonate is the same as that of $\text{BaO} + \text{CO}_2$. G. Y.

Alloys of Magnesium with Cadmium, Zinc, Bismuth, and Antimony. GEORG GRUBE (*Zeit. anorg. Chem.*, 1906, 49, 72—92).—From the results of an investigation of these systems by Tammann's method of thermal analysis, controlled by microscopic observations, the author has obtained evidence of the existence of the following definite crystalline compounds: CdMg , Zn_2Mg , Bi_2Mg_3 , and Sb_2Mg_3 .

The freezing-point curve of the system magnesium—cadmium falls continuously from the melting point of magnesium to that of cadmium, but shows a slight break at 82.19 per cent. by weight of the latter metal, corresponding with the composition of the compound CdMg ; this substance forms a complete series of mixed crystals with both its components. When the cooling is rapid, the crystals separating between 20 and 95 per cent. of cadmium are not homogeneous, owing to equilibrium between the melted alloy and the crystals not being established with sufficient rapidity. There is no evidence of the existence of the compounds CdMg_4 and CdMg_{30} mentioned by Boudouard (*Abstr.*, 1902, ii, 501).

The compound CdMg is greyish-white and slightly harder than cadmium; it becomes oxidised in moist air and is readily acted on by water.

The freezing-point curve of the system magnesium—zinc shows a very distinct maximum at 15.68 per cent. by weight of the former metal, corresponding with the compound MgZn_2 , and two eutectic points at 48.3 and 3.2 per cent. by weight of magnesium respectively; no mixed crystals are formed. Contrary to Boudouard's contention, no compound of the formula ZnMg_4 exists.

Most of the alloys of this system are brittle. The compound MgZn_2 is white, lustrous, and harder than its components; it is not affected by water.

The freezing-point curve of magnesium-bismuth alloys consists of only three branches; there is a well-defined maximum at 710° and 85.09 per cent. by weight of bismuth corresponding with a compound Mg_3Bi_2 , as well as a eutectic point at 552° and 65 per cent. of the last-mentioned metal. The compound Mg_3Bi_2 is practically insoluble in bismuth, so that the freezing point of the latter metal is not affected. No mixed crystals are formed.

The compound Mg_3Bi_2 is steel-grey in colour, very brittle, and becomes slowly oxidised in moist air.

The freezing-point curve of magnesium-antimony alloys shows a well-defined maximum at about 950° and 76.6 per cent. of the latter metal, corresponding with a compound Mg_3Sb_2 , as well as two eutectic points at 627° and 39.5 per cent. and 594° and 97.5 per cent. of antimony respectively; in this case also there is no indication of mixed crystals.

The compound Mg_3Sb_2 forms steel-grey needles and is slowly oxidised in the air. The alloys become more brittle as the proportion of antimony increases. G. S.

Lead and Sulphur. K. FRIEDRICH and A. LEROUX (*Metallurgie*, 1905, 2, 536—539).—The freezing-point curve of mixtures of lead

with lead sulphide has been studied. Pure natural galena was employed, the precipitated sulphide not being found to give a homogeneous product when fused and examined microscopically. Lead sulphide melts at 1103° , and from this point the curve falls without a break. The eutectic horizontal is at 327° , and extends continuously throughout. It was not found possible to determine the position of the lead branch of the curve, which must be very short. Micrographic examination shows the presence of only two constituents, the glistening white crystals of sulphide and the duller lead. The existence of the two lower sulphides, Pb_2S and Pb_4S (Bredberg, 1829), is thus disproved. C. H. D.

Halogen Compounds of Thallium. VICTOR THOMAS (*Compt. rend.*, 1906, **142**, 838—841. Compare Abstr., 1901, ii, 60, 100, 159, 507; 1902, ii, 79, 322; 1903, ii, 147).—The heats of solution of the tetrahydrates of thallium chloride, bromide, and the two chloro-bromo-compounds are respectively -2.1 , $+2.2$, -2.9 , and -2.8 Cal.; the heats of formation of the two last compounds, $TlCl_2Br \cdot 4H_2O$ and $TlClBr_2 \cdot 4H_2O$, from thallic chloride and bromide are 0.6 and 0.7 Cal. respectively, whence it follows that they are definite chemical compounds and not merely isomorphous mixtures.

Chlorine combines with thallous chloride at the temperature of liquid chlorine to form the chloride, Tl_2Cl_3 ; at the ordinary temperature, the dichloride, Tl_2Cl_4 , is formed, whilst in sealed tubes under a pressure of 6 to 7 atmospheres a higher chloride is formed which has not yet been identified. M. A. W.

Solidification of Copper. P. DEJEAN (*Rev. de Métallurgie*, 1906, **3**, 233—242).—The freezing point of pure copper, prepared by de-oxidation of best-selected copper in hydrogen and fusion under charcoal, was found to be 1085° , thus confirming Holborn and Day's value of 1084° (Abstr., 1901, ii, 84). The freezing point is depressed by the addition of cuprous oxide, the eutectic point being reached at 4.7 per cent. of oxide and 1065° (compare Heyn, Abstr., 1904, ii, 406). This was confirmed by micrographic examination. The eutectic point is so well defined as to be a convenient fixed point in the standardisation of pyrometers.

The freezing point of copper is depressed by the addition of aluminium, a temperature of 1039° being reached at 8.6 per cent. of aluminium (compare Guillet, Abstr., 1905, ii, 712). C. H. D.

Red and Blue Modifications of Colloidal Copper. CARL PAAL and WILHELM LEUZE (*Ber.*, 1906, **39**, 1550—1557. Compare Billitzer, Abstr., 1902, ii, 454; Gutbier, Abstr., 1903, ii, 82; Gutbier and Hofmeier, Abstr., 1905, ii, 327).—The reduction of colloidal copper oxide in concentrated solutions (see this vol., ii, 358) by means of hydrazine hydrate leads to the formation of the unstable blue liquid hydrosol, but in warm solutions containing not more than 25 per cent. of copper in presence of a small amount of ammonia to the formation of the stable red liquid hydrosol of copper. Colloidal cuprous hydroxide is formed as an intermediate product. The liquid hydrosol, which is red by transmitted but black by reflected light, and the solid red hydrosol, which is obtained on evaporation of

the solution containing a small excess of hydrazine hydrate, are stable through long periods in the absence of air. When exposed to air, the red liquid hydrosol becomes green, orange, and finally the colour of the colloidal copper oxide solution. The hydrogel of the blue modification is formed when electrolytes are added to the red liquid hydrosol. A hydrosol containing 80 per cent. of copper in combination with lysalbic acid is obtained by careful addition of acetic acid to a solution of red colloidal copper and sodium lysalbate; it is stable when solid, and is insoluble in water, but dissolves in aqueous alkali hydroxides. Red colloidal copper is formed also by reduction of colloidal copper oxide in presence of sodium protalbate or lysalbate by hydrogen at 200°.

The compound of the blue hydrosol with protalbic acid is obtained on careful addition of sulphuric acid to the concentrated solution of colloidal copper oxide and sodium protalbate as a dark copper-coloured, flocculent precipitate, which is readily oxidised by air, and when still moist dissolves in dilute alkali hydroxides, forming a solution which is milky and copper-red by reflected, but deep blue by transmitted light.

G. Y.

Action of Sulphuric Acid on Copper. C. H. SLUITER (*Chem. Centr.*, 1906, i, 903—904; from *Chem. Weekblad.*, 3, 63—66).—The reduction theory affords a better explanation of the action of sulphuric acid on copper than the oxidation theory (compare van Deventer, *Abstr.*, 1905, ii, 383). The formation of copper sulphide can only be rationally accounted for by the assumption that hydrogen is liberated and reduces the sulphur dioxide to hydrogen sulphide. The hypothetical reduction of sulphur dioxide by copper is not supported by any analogous reaction. Further evidence of the formation of hydrogen is afforded by the fact that when a solution of nitrobenzene in sulphuric acid is heated with copper at 130°, aniline is formed. When, however, sulphuric acid containing 12 per cent. of sulphur trioxide is heated with copper at 140°, sulphur dioxide is evolved, but aniline is not formed. E. W. W.

Special Brasses. LÉON GUILLET (*Rev. de Métallurgie*, 1906, 3, 243—288).—Special brasses are industrial alloys of copper and zinc to which a third metal is added. The structure of such alloys generally resembles that of the copper-zinc alloys, but the added metal is equivalent to a certain quantity of zinc, so that the properties of the ternary alloy correspond most closely, not with the copper-zinc alloy containing the proportion of zinc actually present, but with another copper-zinc alloy, containing a different proportion, the “fictitious” proportion of zinc. For instance, an alloy of 70 per cent. of copper, 28 of zinc, and 2 of aluminium does not correspond in properties and micro-structure with one of 70 copper and 30 zinc, but with one of 63.63 copper and 36.37 zinc. The author has determined the “coefficient of equivalence” of a number of metals in thus replacing zinc. Aluminium has the coefficient 6, manganese 0.5, iron 0.9, tin 2, lead 1, silicon 10, and magnesium 2. Antimony does not enter into solid solution, but forms a separate constituent when even small quantities are added. In other cases, a separate constituent does not appear until a considerable quantity of the third metal has been added. When this limit is reached, the rule of equivalence no longer holds good.

The results of Shepherd for copper-zinc alloys (Abstr., 1904, ii, 662) are generally confirmed, but the β solid solutions are found to have a greater range than described by him, extending from 50.5 to 54.75 per cent. of copper. For alloys containing from 54 to 63 per cent. of copper, that is, composed of the α - and β -constituents, the composition can be determined by microscopic examination with an error of 0.5 per cent. or less.

The action of tin in retarding the corrosion of copper-zinc alloys by sea water is attributed to its removing the solid solution β , which is most liable to attack, and replacing it by a highly resistant constituent.

The properties of the alloys examined are tabulated, and the paper contains 59 photo-micrographs. C. H. D.

Alloying of Copper with Pure Iron and Iron-carbon Alloys. V. O. PFEIFFER (*Metallurgie*, 1906, 3, 281—287).—Previous experiments to determine the alloying power of copper with iron have led to very discordant results. The author's experiments, carried out by melting copper with pure iron in a magnesia crucible in an electric furnace, show that no depression of the freezing point of either iron or copper is produced by the addition of the other metal. Microscopic examination confirms the conclusion that iron and copper are mutually insoluble. The supposed alloys described previously are considered to be solidified emulsions; the specific gravity of the two fused metals being nearly equal, and the viscosity of the iron considerable, separation into two layers only takes place very slowly. When sufficient time is allowed for the separation, the copper layer is found to be free from iron.

In similar manner, copper and iron-carbon alloys are found to be mutually insoluble, although finely emulsified mixtures are readily obtained. C. H. D.

Colloidal Copper Oxide. CARL PAAL and WILHELM LEUZE (*Ber.*, 1906, 39, 1545—1549. Compare Paal, Abstr., 1902, ii, 500, 503; Ley, Abstr., 1905, ii, 524).—The deep bluish-violet liquid hydrosol of copper hydroxide is formed when an alkali hydroxide is added to a suspension of copper protalbate or lysalbate. A comparatively concentrated colloidal solution is obtained if further amounts of the copper salt and the alkali hydroxide are added alternately until a permanent precipitate is formed. The colloidal solution always contains small amounts of diffusible copper compounds, and when ammonia is added the diffused solution contains the blue ammoniacal compound of copper hydroxide. During the dialysis, the liquid hydrosol becomes dirty-blue to violet by reflected, brownish-violet to deep brown by transmitted light, perhaps in consequence of dehydration of the colloidal copper hydroxide. On evaporation of the liquid hydrosol in a vacuum, colloidal copper oxide is obtained in stable, brittle, glistening, black or bluish-black scales, which are soluble in water. The adsorption compound of the hydrosol with lysalbic or protalbic acid is precipitated on careful addition of a dilute acid to the colloidal solution. The liquid hydrosol is reduced by hydroxylamine to cuprous oxide, by hydrazine hydrate to colloidal copper. G. Y.

Copper Nitride. ANTOINE GUNTZ and HENRY BASSETT, jun. (*Bull. Soc. chim.*, 1906, [iii], 35, 201—207. Compare Abstr., 1903, ii, 79).—When cuprous oxide, prepared by Russell's method (Abstr., 1894, ii, 93), is heated at 265° in a current of dry ammonia, a green product is formed which consists principally of copper nitride, Cu_3N , but contains in addition small quantities of copper, cuprous chloride (derived from the cuprous oxide used), and ammonia (compare Beilby and Henderson, *Trans.*, 1901, 79, 1253). Hydrochloric acid converts the nitride into cuprous chloride and ammonia. Sulphuric acid behaves similarly, forming cupric sulphate and metallic copper. Nitric acid rapidly oxidises the nitride, only a portion of the nitrogen of the latter being converted into ammonia. Alkalis slowly attack the nitride, forming ammonia and cuprous oxide. T. A. H.

Barium and Mercury Iodides. ANDRÉ DUBOIN (*Compt. rend.*, 1906, 142, 887—889. Compare this vol., ii, 231).—The composition of an aqueous solution saturated with barium and mercuric iodides corresponds with the formula $\text{BaI}_2, 1.33\text{HgI}_2, 7.76\text{H}_2\text{O}$. On cooling this solution, after saturating it with mercuric iodide at 70° , small crystals are obtained of the composition $\text{BaI}_2, 5\text{HgI}_2, 8\text{H}_2\text{O}$, and having the sp. gr. 4.63 at 0° . Occasionally crystals containing 3 mols. of mercuric iodide per 2 mols. of barium iodide separate from the mother liquor. On cooling a solution corresponding with $\text{BaI}_2, 1.30\text{HgI}_2, 10.41\text{H}_2\text{O}$, large prisms of the composition $2\text{BaI}_2, 3\text{HgI}_2, 16\text{H}_2\text{O}$ are deposited; sp. gr. 4 at 0° . When a solution corresponding with $\text{HgI}_2, 1.07\text{BaI}_2, 9.71\text{H}_2\text{O}$ is slowly evaporated over strong sulphuric acid, prismatic crystals of the formula $3\text{BaI}_2, 5\text{HgI}_2, 21\text{H}_2\text{O}$ are obtained; these are very deliquescent, and have a sp. gr. 4.06 at 0° . H. M. D.

Rare Earths. GEORGES URBAIN (*J. Chim. phys.*, 1906, 4, 31—66).—The paper is a *résumé* of the author's work published at intervals since 1899. The first portion deals with a general view of the points of interest and fields for research in connection with the rare earths; the methods of separation are next discussed, and especially the use of a separating compound isomorphous with the salts it is desired to separate (Abstr., 1904, ii, 37, 173). During the separation it is necessary to control the progress of the fractionating from time to time, and methods available are considered; the colour of the salts is at first a sufficient guide, later the absorption and spark spectra of the several consecutive fractions are the best criteria. The method used for the determination of the atomic weight is also briefly discussed (Abstr., 1904, ii, 340, 486). For the determination of the degree of purity, the arc spectrum and the spectrum of the phosphorescence are the most delicate. The method of separation from the crude earths is discussed and the seriation of the elements, the following order of seriation being given: lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium. L. M. J.

Isolation and some Atomic Characteristics of Dysprosium. GEORGES URBAIN (*Compt. rend.*, 1906, 142, 785—788).—Dysprosium,

first isolated by Lecoq de Boisbaudran (Abstr., 1886, 667) from Soret's *X* earth (Abstr., 1878, 629), which Cleve supposed to be the oxide of a new element, holmium (Abstr., 1880, 7), was considered by Krüss and Nilson (Abstr., 1887, 890; 1888, 108, 390), Crookes (Abstr., 1887, 334), and Forsling (Abstr., 1904, ii, 176) to be a mixture of elements; the author has, however, separated 50 grams of an earth from the fractions comprised between the earths of yttrium and terbium by fractional crystallisation of the ethyl sulphates (Urbain, Abstr., 1900, 346), which shows the constant spectrum of dysprosium, and after fourteen crystallisations gives the same mean atomic weight, $D_y = 162.49$, the limits being 162.64 and 162.28. Dysprosium oxide is white and does not form a peroxide, and the salts have characteristic greenish-yellow colour.

M. A. W.

Effect of Calcium in Developing the Phosphorescence of some Rare Earths. Sir WILLIAM CROOKES (*Chem. News*, 1906, 93, 143—144).—It has been suggested by Urbain (compare Abstr., 1905, ii, 458; this vol., ii, 28) that the ultra-violet bands attributed by the author to victorium are due to gadolinium, which, whilst not exhibiting the bands in the pure state, does so in presence of an exciting element. Measurements with an instrument of large dispersion indicate, however, that the main band of victorium which extends from $\lambda 3115.2$ to $\lambda 3120.7$ is double, the centres of its two components being at $\lambda 3116.6$ and $\lambda 3119.5$, whilst the gadolinium-calcium bands occur between $\lambda 3136$ and $\lambda 3155$. When calcium oxide was added to Urbain's pure europia, the faintest trace of the victorium bands was discernible, but no effect was produced in the case of Urbain's pure gadolinia. When, however, the oxides were converted into sulphates, distinct bands of the same wave-length and character as the victorium bands were observed.

Mixtures containing different proportions of victorium and calcium were also examined in the form of the oxides and also of the sulphates. In the case of the oxides, it was found that the victorium group of bands is strongest in the mixtures containing the smallest proportion of victorium, whilst in the case of the sulphate mixtures the reverse effect is obtained. From the observations the author concludes that the victorium bands cannot be attributed to gadolinium *plus* an exciting element.

H. M. D.

Phosphorescence (Cathode-luminescence) Spectra of Rare Earths and the New Elements Ionium, Incognitum, and Victorium. ROBERT MARC (*Ber.*, 1906, 39, 1392—1395).—In the light of his own researches (Abstr., 1901, ii, 634), the author adversely criticises Crookes' phosphorescence method for the detection of new elements (Abstr., 1899, ii, 751; 1905, ii, 250). The existence of victorium is denied by Urbain (this vol., ii, 28).

C. S.

Spectroscopic Investigation of Urbain's Terbium Preparations. G. EBERHARD (*Sitzungsber. K. Akad. Wiss. Berlin*, 1906, 384—404).—Measurements of the wave-length and intensity of a large number of lines in the terbium spectrum in Urbain's prepara-

tions (Abstr., 1905, ii, 711) indicate that terbium is a well-defined element with a characteristic spectrum, and that it shows no signs of a fractional separation into other elements. Spectroscopic evidence is against there being an element between gadolinium and terbium. Many of the terbium lines can be used to indicate the presence of this element in minerals; they are not present in the solar spectrum.

E. F. A.

Atomic Weight and Spark Spectrum of Terbium. GEORGES URBAIN (*Compt. rend.*, 1906, 142, 957—959. Compare Abstr., 1905, ii, 711).—The hydrated terbium sulphate, $\text{Tb}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, used in determining the atomic weight of terbium forms crystals which are stable in dry air at the ordinary temperature, and become completely anhydrous at 360° ; the atomic weight of terbium determined from five different fractions is 159.22 ($\text{O} = 16$), the limiting values being 159.30 and 159.17.

The spark spectrum of terbium is very rich in rays, and the original contains a list of thirty-seven characteristic lines between $\lambda = 3053.6$ and $\lambda = 3874.6$, seven of which were attributed by Demargay to the element Γ (Abstr., 1900, ii, 656).

M. A. W.

Alloys of Nickel and Antimony. K. LOSSEW (*Zeit. anorg. Chem.*, 1906, 49, 58—71).—From the results of an investigation of this system by Tammann's method of thermal analysis, controlled by microscopic observations, the author draws the conclusion that nickel forms the following four compounds with antimony: NiSb , Ni_5Sb_2 , Ni_4Sb_5 , and Ni_4Sb ; the evidence for the existence of Ni_4Sb_5 is, however, not quite conclusive.

The freezing-point curve shows two maxima at 1158° and 32.83 per cent. and 1170° and 55 per cent. by weight of nickel respectively, corresponding with the compounds NiSb and Ni_5Sb_2 , and there are three eutectic points at 2—3, 47.6, and 66.1 per cent. by weight of nickel respectively. From 32.8—40 per cent., 55—57 per cent., and 92.5—100 per cent. of nickel, mixed crystals separate out. In the alloys with from 3—32.8 per cent. of nickel, microscopic observation shows a third crystalline form in addition to the compound NiSb and the eutectic mixture; there are indications that these crystals represent another compound, Ni_4Sb_5 , but conclusive evidence on this point could not be obtained. From 57—92.5 per cent. of nickel, the two series of saturated mixed crystals existing within these limits interact when the temperature falls to 677° with formation of a third definite compound, Ni_4Sb ; this reaction proceeds in the reverse direction at higher temperatures.

The compound NiSb is copper-red in colour, hard and brittle; the compound Ni_5Sb_2 has a grey colour and is harder, but not so brittle as the former.

The alloys from 57—100 per cent. by weight of nickel are magnetic; the temperatures at which the magnetism disappears on heating are given.

The paper is illustrated by microphotographs.

G. S.

Silicides of Nickel. W. GUERTLER and GUSTAV TAMMANN (*Zeit. anorg. Chem.*, 1906, **49**, 93—112. Compare this vol., ii, 32).—From the results of their investigation of this system by Tammann's method of thermal analysis, controlled by microscopic observations, the authors draw the conclusion that five compounds of these two elements exist, the respective formulæ of which are: Ni_3Si , Ni_2Si , Ni_3Si_2 , NiSi , and Ni_2Si_3 .

The freezing-point curve of the system shows two maxima at 33·3 and 50 atom. per cent. of silicon respectively, corresponding with the compounds Ni_2Si and NiSi , as well as three eutectic points at 20, 43, and 56 atom. per cent. of silicon respectively. From 0—11·6 and 27·6—33·3 per cent. of silicon, two series of mixed crystals separate; if allowed to cool slowly, the saturated crystals interact below 1125° (in alloys containing 11·6—27·6 per cent. of silicon) with formation of a third compound, Ni_3Si ; the reaction is a reversible one. A third series of mixed crystals separates from 33·3—37·5 atom. per cent. of silicon; if the cooling is slow, a fourth compound, Ni_3Si_2 , is formed from these when the temperature falls below 830°. The existence of the remaining compound, Ni_2Si_3 , was proved by thermal analysis; it is formed on cooling by interaction of silicon and the fused mass containing 59 atom. per cent. of the latter element.

The alloys from 0—20 per cent. of silicon are fairly tough; beyond this point they are brittle and easily powdered. Between the limits of 5 and 20 per cent. of silicon, the alloys are fairly hard, but, contrary to the behaviour of carbon steel, the rapidly cooled alloys are much softer than those allowed to cool slowly. From 20 atom. per cent. of silicon, the hardness gradually decreases, reaches a minimum about 70 per cent., and beyond this point rapidly increases. Alloys containing more than 30 atom. per cent. of silicon are no longer magnetic.

The paper is illustrated by microphotographs.

G. S.

Influence of Foreign Elements on the Separation of Graphite from Cast Iron. F. WÜST (*Metallurgie*, 1906, **3**, 169—175, 201—205. Compare Wüst and Geiger, this vol., ii, 88).—A pure cast iron, containing 3·96 per cent. of carbon, was melted, and weighed quantities of the foreign element added. After casting, care being taken to ensure uniformity of conditions, the alloy was analysed. The ratio of graphite to total carbon was then plotted against the percentage of added foreign element.

[With JOS. KREITEN.]—The presence of tin reduces the solubility of carbon in pure iron, and therefore increases the separation of graphite. The separation of graphite due to silicon is not affected by the addition of tin. In the presence of an excess of carbon, iron can dissolve a maximum of 16 per cent. of tin.

[With P. PÜTZ.]—The addition of sulphur reduces the solubility of carbon in iron, but does not cause the conversion of combined carbon into graphite. The effect of silicon in causing graphite to separate is neutralised by the addition of sulphur.

Phosphorus is without influence on the carbon in silicon-free iron so long as the proportion of phosphorus does not exceed 2·5 per cent.;

larger quantities produce a proportional separation of graphite. In the presence of 0.9 per cent. of silicon, 3 per cent. of phosphorus and upwards causes separation of graphite.

C. H. D.

Reduction of Ferrous Oxide and the Three Modifications of Carbon. RUDOLF SCHENCK (*Zeit. Elektrochem.*, 1906, 12, 218—220).—A reply to Baur's criticisms of a paper by Schenck and Heller (*Abstr.*, 1905, ii, 519).

T. E.

Electrolytic Formation of Chromium. OCTAVE DONY-HÉNAULT (*Zeit. Elektrochem.*, 1906, 12, 329—330).—Referring to Carveth and Mott's work (*Abstr.*, 1905, ii, 394), the author considers that the formation of chromous salt is not the only condition required for the deposition of metallic chromium from a solution of a chromic salt. In some experiments with solutions of chrome-alum, he found that after electrolysis had gone on for a short time the green solution became violet, and after a time deposited violet crystals of the alum. Chromium was deposited from the violet, but not from the green solutions.

T. E.

Chromium Chlorosulphates. NIELS BJERRUM (*Ber.*, 1906, 39, 1597—1602. Compare Werner and Huber, this vol., ii, 170; Weinland and Krebs, *ibid.*, 233).—The formula suggested by Werner and Huber for the salt isomeric with Recoura's chromium chlorosulphate is in complete accord with the fact that when a solution of the salt in dilute hydrochloric acid is saturated with hydrogen chloride a precipitate of violet chromic chloride is obtained, which contains 50 per cent. of the total chromium originally present. A new chromic chloride, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, the hitherto unknown chlorochromium dichloride, is obtained when the violet chloride contained in a boiled solution of the green chloride is precipitated with hydrogen chloride, and the filtrate then mixed with a large volume of ether saturated with hydrogen chloride. It may be recrystallised by solution in a mixture of equal volumes of ether and concentrated hydrochloric acid, and then pouring into ether saturated with hydrogen chloride. When freshly prepared, only two-thirds of the chloride can be precipitated by means of silver nitrate. The same salt is also formed (75 per cent. yield) when Recoura's chromium chlorosulphate is dissolved in hydrochloric acid and then poured into a large excess of ether saturated with hydrogen chloride. When a solution of the new chloride is mixed with concentrated sulphuric acid, Recoura's salt is obtained, and the latter would thus appear to be chlorochromic sulphate, $[\text{ClCr}]\text{SO}_4$. The conductivity and the alteration of the conductivities of the two chlorosulphates agree with the formulæ suggested.

Weinland and Krebs' conclusion that the whole of the SO_4 in the two salts described by them is united in the form of a complex is not accepted, since even extremely dilute acidified solutions of potassium sulphate do not yield an immediate precipitate with barium chloride. The molecular depressions of the freezing points for various sulphates are compared, and they are of much the same order as that obtained by Weinland and Krebs for the green chlorosulphate.

J. J. S.

Constitution of Chromic Acid. WILHELM MANCHOT [and, in part, R. KRAUS] (*Ber.*, 1906, **39**, 1352—1356).—From the experiments quoted on the oxidation of uranous salts with chromic acid under conditions previously described by the author for iron and titanium salts (*Abstr.*, 1903, ii, 152; this vol., ii, 172), the conclusion is drawn that three equivalents of oxygen are required during the oxidation of one atom of uranium, two equivalents being required by the uranium and one by the hydriodic acid present.

The constitution of chromic anhydride is discussed. The formula $\text{O}:\text{Cr}\begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$ is regarded as untenable. The formulæ $\text{O}:\text{Cr}\begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$ for the anhydride and $\begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix} > \text{Cr} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$ for the acid are suggested, amongst the evidence submitted in favour of the latter formulæ being the fact that a little ozone is produced when potassium dichromate is heated with concentrated sulphuric acid.

The first phase during the oxidation of any substance by chromic acid consists in the addition of the chromic acid to form a compound of the nature of a peroxide with the substance acted on.

A. McK.

Behaviour of Sulphur towards Potassium Chromate and Dichromate. KAMILLO BRÜCKNER (*Monatsh.*, 1906, **27**, 199—204. Compare Lassaigue, *Ann. Chim. Phys.*, 1820, [ii], **14**, 299; Döpping, *Annalen*, 1843, **46**, 172).—When heated with sulphur in air, chromium oxide remains unchanged; chromium trioxide inflames and forms chromium oxide, together with a small amount of chromium sulphide, whilst potassium chrome alum, if the heating is prolonged, forms chromium oxide and potassium sulphate only, but if the heating is limited these are accompanied by a compound of chromium and potassium sulphides, which is insoluble in water, but is decomposed by hydrochloric or nitric acid.

When heated for a limited time with an excess of sulphur, potassium chromate forms potassium sulphide, sulphate, and chromate, chromium oxide, and the compound of chromium and potassium sulphides; if the heating is continued until the sulphur is completely volatilised, the product contains potassium sulphate and chromate, chromium oxide, and a small amount of the chromium and potassium sulphide compound; whilst if the mixture is more strongly heated, potassium sulphate and chromium oxide with only traces of chromium sulphide and of chromates are obtained.

Potassium dichromate reacts in a similar manner, but in consequence of the larger proportion of oxygen present the reaction resembles also that of chromium trioxide and sulphur.

It is probable that potassium sulphide and thiosulphate and chromium oxide and sulphide are the immediate products of the interaction of potassium chromate or dichromate and sulphur.

G. Y.

Compounds of Iron and Molybdenum. ÉMILE VIGOUROUX (*Compt. rend.*, 1906, **142**, 889—891, 928—930).—Definite compounds

of iron and molybdenum have been obtained by reducing mixtures of the two oxides by the Goldschmidt method, and also by heating mixtures of the finely-divided metals at high temperatures in a stream of hydrogen. The compounds Fe_2Mo , Fe_3Mo_2 , FeMo , and FeMo_2 were isolated. They are grey and crystalline, non-magnetic, insoluble in hydrochloric acid, but readily dissolved by nitric acid. Contraction takes place in their formation. Free iron was found in the solidified mass of metal whichever of the above compounds was formed, but this could be easily removed by means of hydrochloric acid.

The compound Fe_2Mo is obtained from alloys containing less than 46.16 per cent. of molybdenum; it has the sp. gr. 8.90 at 0° . Chlorine attacks the compound slowly at the ordinary temperature, vigorously at 250° ; oxygen, sulphur, and water vapour react at a red heat. Solutions of hydrochloric and hydrofluoric acids, as well as gaseous hydrogen chloride, have no appreciable action, but the compound is readily attacked by hot concentrated sulphuric acid, by dilute nitric acid, and by iodine suspended in water. Potassium hydroxide has no action in solution, but reacts readily in the fused condition.

Fe_3Mo_2 is separated from alloys containing about 50 per cent. of molybdenum; it has the sp. gr. 9.16 at 0° , and it behaves towards reagents in a similar manner to Fe_2Mo .

FeMo separates from alloys containing 54–63 per cent. of molybdenum; it has the sp. gr. 9.01 at 0° . It becomes incandescent in chlorine at 285° , and in oxygen at a red heat.

FeMo_2 is obtained from alloys containing 64–77 per cent. of molybdenum; it has the sp. gr. 9.41 at 0° . Chlorine attacks it with incandescence at 305° , oxygen at 350° ; sulphur has very little action, and aqueous iodine reacts very slowly.

When an alloy containing 77.8 per cent. of molybdenum is heated in a current of hydrogen chloride, it is found that the whole of the iron can be separated from the molybdenum.

H. M. D.

Electrolytic Reduction of Molybdic Acid in Acid Solutions

III. ALBERTO CHILESOTTI (*Zeit. Elektrochem.*, 1906, 12, 197–208. Compare this vol., ii, 263).—Measurements of the potentials of the cathodes used in the experiments previously described are given. The conclusion drawn from the measurements is that the differences between cathodes of different metals cannot be accounted for by any single hypothesis. The potential of a cathode of lead or of tin is that required to discharge ions of the metal, the reduction being apparently due to the action of the metal which dissolves. Mercury and smooth platinum cathodes behave in the same way, the cathodic potential first increasing to a maximum, which is reached, roughly speaking, when the molybdenum has been reduced to the quinquevalent condition. The potential then falls more or less, finally increasing again, when the molybdenum is practically completely reduced to the trivalent stage. To explain these changes, it is necessary to assume that a deposit (probably of molybdenum) is formed on the cathode in the early stages of the reaction, which retards the reduction; this disappears later, and a little bivalent molybdenum salt is formed in the solution, both of which changes accelerate the

reduction and lower the potential. At a platinised platinum cathode, the reduction to quinquivalent molybdenum proceeds quantitatively at a very low potential; this necessitates the assumption of a catalytic action of the platinum black. T. E.

Distillation of Titanium, and the Temperature of the Sun. HENRI MOISSAN (*Compt. rend.*, 1906, 142, 673—677. Compare this vol., ii, 92, 175, 232).—When titanium, containing 2 per cent. of carbon (Abstr., 1895, ii, 272), is heated in the electric furnace with a current of 500 amperes and 110 volts for five minutes, the metal is only superficially fused, and the loss of weight by distillation is less than 2 per cent.; if, however, a current of 1000 amperes and 55 volts is employed, the titanium is completely fused and 36 per cent. can be distilled in seven minutes. The distillate consists of minute crystals of titanium together with yellow crystals of titanium nitride and of lime, whilst near the orifice of the furnace blue crystals of the protoxide are found.

The author has shown that titanium, iron, chromium, manganese, and tungsten can be distilled in the electric furnace at a temperature of about 3500° under atmospheric pressure, and as these metals all exist in a state of vapour in the sun, the temperature of the sun is probably nearer 2000° to 3000° (compare Violle, *Compt. rend.*, 1874, 78, 1425, 1816; 79, 746; 1876, 82, 662, 729, 896) than 6590° (compare Wilson, *Proc. Roy. Soc.*, 1902, 69, 312).

M. A. W.

Electrolytic Preparation and Properties of Vanadous and Vanadic Salts. T. F. RUTTER (*Zeit. Elektrochem.*, 1906, 12, 230—231).—The reduction of vanadic acid to vanadous sulphate takes place much more easily at a mercury cathode than at a platinum cathode (compare Piccini and Marino, Abstr., 1902, ii, 663). A solution of vanadous sulphate reduces silver bromide to the metal. The reduction of silver from a solution of the sulphate furnishes a very delicate test for vanadous salts; the sensitiveness of the test is much increased by adding a drop of a solution of copper sulphate after adding the silver solution.

The reduction of vanadic acid to a vanadic salt is readily carried out by using a platinised platinum cathode, no vanadous salt being produced. The oxidation of vanadic salts by oxygen or by silver sulphate is accelerated by copper sulphate. Copper sulphate itself is not reduced to copper. T. E.

Antimony Sulphide and Antimony. PAUL CHRÉTIEN and JOSEPH GUINCHANT (*Compt. rend.*, 1906, 142, 709—711. Compare Abstr., 1904, ii, 538; Pélabon, Abstr., 1904, ii, 267; this vol., ii, 173).—The formation of two liquid phases when mixtures of antimony and antimony sulphide are fused (Pélabon, Abstr., 1904, ii, 267) is associated with the facts that the sulphide has a lower density than the metal and a higher coefficient of expansion; antimony has a sp. gr. 6.75 at 13°, 6.55 at 698°, and 6.45 at 1156°, whilst stibnite has a sp. gr. 4.63 at 13°, 3.85 at 643°, and 3.82 at 1116°. The authors have

determined the solubility of antimony in the sulphide, and find that the quantity p of antimony which is dissolved in 100 grams of the mixture is a function of the temperature, and can be represented approximately by the two straight lines:

$$p = 20.33 + (t - 810)/30 \quad \text{for temperatures below } 810^{\circ}.$$

$$p = 20.33 + 3(t - 810)/1000 \quad \text{,, ,, above } 810^{\circ}.$$

The experiments were made by heating excess of antimony with the sulphide for one hour at the temperature of observation, and removing a portion of the upper liquid layer for analysis by means of a cooled copper tube, or by fusing the mixture in a quartz tube, cooling it suddenly in cold water, breaking the tube, and removing the upper sulphide layer for analysis.

M. A. W.

Alloys of Antimony and Tin. F. E. GALLAGHER (*J. Physical Chem.*, 1906, 10, 93—98).—The freezing-point curve for alloys of antimony and tin was investigated by Reinders (Abstr., 1900, ii, 731), who found transition points at 243° , 310° , and 430° . The author's results yield 319° for the second point, and the cause of the error in Reinders' work is considered to be a too rapid rate of cooling. The author finds that no compounds of tin and antimony exist, but that the four solid phases are solid solutions which the author terms the α -, β -, γ -, and δ -crystals, beginning at the antimony end of the freezing-point curve. The equilibrium diagram is given, which shows the yields for the different crystals. The β -crystals are unstable below 319° in presence of the fused mass, and below 313° in presence of α -crystals.

L. M. J.

Determination of the Absolute Atomic Weight of Bismuth. GUSTAV D. HINRICHS (*Chem. Centr.*, 1906, i, 1083; from *Mon. Sci.*, [iv], 20, i, 169—174).—The author's method of calculating the "absolute" or true atomic weight is applied in this paper, by way of example, to the case of bismuth, the most recent determinations of Birkenbach and Gutbier being considered in this connection.

E. W. W.

Production of Gold Hydrosols by Ethereal Oils. LUDWIG VANINO and F. HARTL (*Ber.*, 1906, 39, 1696—1700. Compare Abstr., 1905, ii, 171).—When small quantities of oil of turpentine (or pinene), or, less efficiently, oil of rosemary, are added to aqueous solutions containing not more than 0.0181 per cent. of gold, hydrosols are formed, the colours of which depend on the temperature and concentration. The formaldehyde in Zsigmondy's experiments can be replaced by oil of turpentine.

The formation of these gold hydrosols is accelerated by inoculation, that is, the addition of one drop of a prepared hydrosol to the solution of gold chloride; the colour of the resultant liquid is, *ceteris paribus*, affected by inoculation.

C. S.

Mineralogical Chemistry.

Crystallised Sulphur from the Muschelkalk of Bruchsal, Baden. KARL BEIERLE (*Centr. Min.*, 1906, 202—205).—Transparent, sharply-developed crystals of sulphur, 1 cm. in length, occur in crevices and cavities in bituminous limestone in a quarry near Bruchsal; they encrust crystals of calcite, and are themselves encrusted with numerous minute crystals of pyrites. A crystallographic description is given. The crystals were doubtless deposited by hydrogen sulphide formed by the reducing action of organic matter on the decomposition products of the pyrites contained in the surrounding rock. L. J. S.

Optical Activity and Origin of Mineral Oil. PAUL WALDEN (*Chem. Zeit.*, 1906, 30, 391—393).—The author considers the origin of the optically active naphthenes from inorganic sources to be impossible, and is of opinion that they have been produced by the decomposition of plant remains. P. H.

Structure and Probable Origin of the Magnetic Iron Ore of Diélette, Manche. L. CAYEUX (*Compt. rend.*, 1906, 142, 716—718).—From a micrographical study of the magnetic iron ore of Diélette the author finds that the rock was originally oolitic and that the primitive structure has been almost completely effaced by the development of magnetite. M. A. W.

Formation of an Iron Mineral by the Decomposition of Glauconite. L. CAYEUX (*Compt. rend.*, 1906, 142, 895—897).—Microscopic examination of the glauconite and limonite grains in the ferruginous mineral found at Grandpré (Ardennes) shows with certainty that the limonite has been produced by transformation of the glauconite which originally formed the chief mineral constituent of the deposit. H. M. D.

Minerals from Val d'Aosta. FEDERICO MILLOSEVICH (*Atti R. Accad. Lincei*, 1906, [v], 15, 317—321).—(1) Rhodochrosite occurs at S. Barthélemy in violet-red crystals resembling the rhombohedral carbonates. Analysis gave:

MnO.	FeO.	CaO.	MgO.	CO ₂ .
56.0	2.04	3.33	traces	38.63

The crystals are often accompanied by others of quartz and albite. Manganese carbonate occurs also in an amorphous form at S. Barthélemy.

(2) Crystallised gold from Pralorgnan (S. Marcel) is found in crystals up to 1 mm. in diameter and exhibits the form {211}, the occurrence of which Dana states to be uncertain.

(3) Titaniferous hæmatite from Pralorgnan (S. Marcel) occurs associated with auriferous albite and sometimes in the crystalline state.
T. H. P.

Composition of Kleinite. ARTHUR SACHS (*Centr. Min.*, 1906, 200—202).—In the undetermined mercury oxychloride mentioned by A. J. Moses (Abstr., 1904, ii, 46), W. F. Hillebrand (*Amer. J. Sci.*, 1906, 21, 85) has determined the presence of nitrogen and sulphuric acid. Kleinite (this vol., ii, 176), having been suggested to be identical with the same mineral, has been re-examined, and nitrogen and sulphuric acid determined with the following results :

	NH ₃ .	SO ₃ .
I. Sulphur-yellow variety	0.44	1.05
II. " " "	1.09	0.85
III. Orange-coloured ,,	2.79	2.57

It is suggested that these variable and non-essential constituents replace oxygen and chlorine respectively, and the formula is written as $\text{Hg}_4[\text{Cl}(\text{SO}_4)_{\frac{1}{2}}]_2[\text{O}(\text{NH}_2)_2]_3$.
L. J. S.

Chalybite and Barytes from Maryland. WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1906, [iv], 21, 364—370).—A crystallographic description is given of chalybite and barytes, which occur associated together at Frostburg, Maryland. The chalybite is in minute, brown crystals with a brilliant iridescent tarnish: the habit is scalenohedral, $v \{20\bar{1}\}$, and the vertical axis $c = 0.8241$. Analysis gave ferrous oxide 62.01 per cent., and an absence of calcium, magnesium, and manganese.
L. J. S.

Crystalline Form of Cabrerite. ARTHUR SACHS (*Centr. Min.*, 1906, 198—200).—Annabergite ($\text{Ni}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$) has not been observed in distinct crystals: crystallographic determinations are now given of the magnesian variety, cabrerite, which occurs as apple-green crystals in grey limestone at Laurion, in Greece. The crystals are monoclinic and have a perfect cleavage parallel to the plane of symmetry [$a : b : c = 0.8239 : 1 : 0.7767$; $\beta = 106^\circ 29'$]; the mineral is therefore isomorphous with vivianite and erythrite. Analysis gave :

As ₂ O ₅ .	NiO.	CoO.	FeO.	MgO.	H ₂ O.	Total.	Sp. gr.
40.45	26.97	trace	1.10	6.16	25.26	99.94	3.01

L. J. S.

Scheelite from Traversella. LUIGI COLOMBA (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 281—290).—The author describes various varieties of scheelite from Traversella, some of them exhibiting forms not previously observed on scheelite crystals. The following table contains analyses of four specimens, in all of which, however, are small quantities of Di_2O_3 and Ce_2O_3 , these being calculated with the lime :

	WO ₃ .	MoO ₃ .	CaO.	MgO.	Total.
Colourless	77.03	3.15	19.73	—	99.91
Reddish-brown ...	77.35	2.46	18.33	1.67	99.81
Greenish-brown ...	78.75	1.47	19.23	0.55	100.00
Orange-yellow	79.68	0.72	19.43	trace	99.83

T. H. P.

Monazitic Sand from Queensland (*Bull. Imp. Inst.*, 1905, 3, 233—236).—On concentrating the crude sand by means of running water, a considerable amount of quartz, felspar, biotite mica, actinolite, and other rock-fragments was removed, and the residue formed about 21 per cent. of the original weight. The concentrated material gave the following results: SiO₂, 7.59; TiO₂, 44.59; ZrO₂, 1.06; ThO₂, 0.23; Al₂O₃, 1.46; Y₂O₃, 0.10; Fe₂O₃, 1.24; FeO, 36.38; MnO, 2.79; CuO, 0.05; CaO, 0.79; MgO, 1.16; CeO, 0.46; P₂O₅, 0.41; Cb₂O₅ and Ta₂O₅, 0.78; H₂O, 0.80. From these results and microscopical examination, the proximate composition of the concentrated mineral was as follows: ilmenite, 84.0; magnetite, 1.8; zircon, 1.4; quartz, 4.4; garnet and other silicates containing alumina, lime, and magnesia, 5.0; monazite, 1.2; tantalite, 0.9; moisture, 0.8. E. G.

Constitution of Titanite. FERRUCCIO ZAMBONINI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 291—295).—After referring to the various formulæ previously ascribed to titanite, the author points out that all recent investigations on titanium and on the neighbouring elements zirconium and tin indicate that these elements readily form complex anions. The conclusion is drawn that titanite is the calcium salt of a complex titanosilicic acid, TiO:O₂:Si:O₂Ca, and that in those varieties which contain iron, aluminium, ytterbium, and cerium, the bivalent group TiO is probably replaced by two univalent groups, RO; analyses show, indeed, that when one of these other metals is present, the amount of titanium is lowered. T. H. P.

Chemical Composition of Glaucosite. LÉON W. COLLET and GABRIEL W. LEE (*Compt. rend.*, 1906, 142, 999—1001. Compare Clarke, *Abstr.*, 1904, ii, 134).—A fresh sample of marine glaucosite from Sir John Murray's collection has the following composition:

SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	MnO ₂ .	FeO.	MgO.	K ₂ O.	H ₂ O.
47.46	30.83	1.53	traces	3.10	2.41	7.76	7.00

and is therefore a ferric and not a ferrous silicate. M. A. W.

Stony Meteorite from Coon Butte, Arizona. JOHN W. MALLET (*Amer. J. Sci.*, 1906, [iv], 21, 347—355).—A meteoric stone weighing 2789 grams was found at Coon Butte, in Coconino Co., Arizona, in June, 1905; a meteoritic fall was observed in this locality about January 15th, 1904. The sp. gr. of the mass is 3.471. The structure is indistinctly chondritic and brecciated, like that of the Pultusk meteorites. Thin sections show, in addition of olivine, enstatite, &c., a colourless isotropic substance which is probably maskelynite. From

the analytical results, the following mineralogical composition is deduced: enstatite, 44.73; olivine, 33.48; maskelynite (?), 6.87; nickel-iron, 8.63; iron-rust, 3.03; schreibersite, 0.76; pyrrhotite, 2.14; chromite, 0.08 per cent. The nickel-iron has the following composition:

Fe.	Ni.	Co.	Cu.	Sn.	Mn.	C.	Total.
88.81	10.72	0.15	trace	0.01	trace	trace	99.69

L. J. S.

New Stony Meteorite from Modoc, Kansas. GEORGE P. MERRILL and WIRT TASSIN (*Amer. J. Sci.*, 1906, [iv], 21, 356—360).—This meteorite was observed to fall at Modoc, in Scott Co., Kansas, on September 2nd, 1905. Several complete stones and some fragments were picked up over an area of two by seven miles; the largest weighs 4640 grams. Sp. gr. 3.54. The structure is chondritic, and the material is traversed by thread-like black veins. The following composition of the stone is calculated from the analyses of the metallic portion and of the soluble and insoluble silicates:

Fe.	Ni.	Co.	S.	P.	SiO ₂ .	FeO.	MnO.
6.56	0.68	0.034	1.38	0.051	44.13	15.37	0.10
	CaO.	MgO.	Al ₂ O ₃ .	K ₂ O.	Na ₂ O.	Total.	
	1.74	26.45	2.47	trace	0.44	99.40	

The corresponding mineralogical composition is: nickel-iron, 4.59; troilite, 3.79; schreibersite, 0.34; olivine, 46.40; enstatite, 29.94; other insoluble silicates (felspar, &c.), 14.36 per cent. L. J. S.

Physiological Chemistry.

Rôle of Oxygen in Artificial Parthenogenesis and Development. JACQUES LOEB (*Univ. Calif. Publ. Physiol.*, 1906, 3, 33—37, 39—47, 49—56).—A series of papers on the part played by oxygen in the processes of the developing eggs of the sea urchin. The toxic effects of sea water rendered hypertonic by the addition of sodium chloride, calcium chloride, or sugar can be prevented for a time by lack of oxygen. This harmonises with the idea that such solutions accelerate or modify oxidation (and possibly other catalytic processes), and that their destructive effect is due to this influence. Hypertonic solutions cause artificial parthenogenesis by accelerating in the resting egg the process of oxidation, which is intimately connected with the synthesis of nuclein from protoplasmic material. The presence of free oxygen in the water is necessary for the production of artificial parthenogenesis.

W. D. H.

Reaction of the Blood; its Function in Nutrition. JEAN GAUTRELET (*Compt. rend.*, 1906, 142, 659—662).—The conclusion drawn from the observations recorded is that there is a parallelism between the “apparent” alkalinity of the blood and the activity of organic exchanges as measured by the amount of hæmoglobin.

W. D. H.

Viscosity of Blood. RUSSELL BURTON-OPITZ (*Pflüger's Archiv*, 1906, 112, 189—193. Compare Abstr., 1905, ii, 98).—The viscosity of blood is influenced by changes of its temperature both *in vitro* and *in vivo*. In the present research, a febrile condition was produced in dogs by the introduction of *Staphylococcus pyogenes aureus*, but in spite of the high body temperature the viscosity of the blood increases, although the specific gravity falls.

Phenylhydrazine is a poison which dissolves the red corpuscles, and therefore presumably should lower the viscosity and specific gravity. The blood of dogs who had received a dose of this drug subcutaneously had a low, sometimes very low, specific gravity. The viscosity was sometimes lessened also, but in the animal whose blood had the lowest specific gravity the viscosity was increased. The specific gravity is no criterion of the viscosity.

W. D. H.

Blood Coagulation. LEO LOEB (*Beitr. Chem. Physiol. Path.*, 1906, 8, 67—94. Compare Abstr., 1904, ii, 496, 747; 1905, ii, 330).—The observations again relate to the blood of invertebrates. Active thrombin solutions are obtained by pressing out the serum after the second coagulation is concluded. The active substance is extracted from the corpuscles; after removal of the corpuscles, spontaneously-coagulating lobster blood does not contain thrombin in appreciable amount. Thrombin and prothrombin cannot be obtained from the cells of blood which has been kept on ice. This probably depends on the direct influence of the cold on the cells; they remain contracted, and do not exhibit the changes they usually do when blood is shed. Prothrombin is not present in appreciable quantity in the circulating blood. Cold also inhibits the activity of thrombin and of the tissue coagulins (the thrombokinasases of Morawitz) when they are added to plasma.

The substance in muscle which hastens blood clotting is only slowly extracted; the substance with the opposite action is rapidly extracted. The latter substance acts feebly or not at all on thrombin, but is strongly inhibitory to the coagulins. It can, therefore, be used to differentiate between them. It is not destroyed by boiling, and its action can in great measure be neutralised by calcium or magnesium chloride. It is present in many tissues, but mainly in the muscles. The influence of various factors and reagents on the action of the ferment and the coagulins is described at length, special interest attaching to the influence of calcium salts. The view that the coagulin alters the fibrinogen and then that calcium reacts with the altered fibrinogen is not supported. During clotting, a great part of the thrombin is rendered inactive; the tissue coagulins form no fresh thrombin, but act directly on fibrinogen. The substance which hastens coagulation which is present in the tissues is different from

that present in the blood, and the former is not changed into the latter (thrombin) by the agency of calcium salts. W. D. H.

The Nucleus of Birds' Red Corpuscles. M. PIETTRE and ANTONY VILA (*Compt. rend.*, 1906, 142, 908—910).—The corpuscles were obtained from the defibrinated blood of pigeons and fowls, washed by centrifugalising with salt solution, and their nuclei liberated by the addition of dilute acetic acid. The nuclei were finally separated in the centrifuge, and washed in the filter with distilled water. The percentage numbers obtained by analysing the dry product were: C, 48.0—49.8; H, 6.56—6.77; N, 15.51—15.94; P, 2.5—3.24; ash, 3.35—3.81.

Attention is directed to the high percentage of phosphorus, most of which is combined organically; it is nearly ten times as abundant as iron in hæmoglobin. W. D. H.

Anti-oxydasic Serum. C. GESSARD (*Compt. rend.*, 1906, 142, 641—642).—If rabbits are immunised with oxydases obtained from certain mushrooms, they yield an anti-oxydasic serum. W. D. H.

Influence of Barium and Radium Bromides on Proteid Metabolism. W. N. BERG and W. H. WELKER (*J. Biol. Chem.*, 1906, 1, 371—412).—Numerous previous observations on the toxicity of barium bromide are confirmed. Radium preparations of low activity containing barium bromide in predominating proportions have no special influence on metabolism when given by the mouth or subcutaneously in relatively large quantities. Equal or larger doses of pure barium bromide have also no decisive effects until fatal results are inaugurated. After subcutaneous injection, radium (bromide), like barium, calcium, and similar elements, is eliminated *per rectum*. Elimination occurs speedily, and the intestine is the main channel of excretion. It is eliminated slightly by the urine, but not by skin glands or epidermis. W. D. H.

Influence of Alcohol on the Activity of the Pancreatic Enzymes. A. GIZELT (*Pflüger's Archiv*, 1906, 111, 620—637).—The experiments were made on dogs with pancreatic fistula. Introduction of alcohol into the intestine usually produces an increased flow of the juice if the two vagi are intact. The introduction of alcohol into the blood stream has no effect; it then manifests only its narcotic properties; but if introduced subcutaneously it increases pancreatic activity. It is believed to act on the medullary centres which govern pancreatic secretion. The juice secreted has less power to digest proteids, fats, and carbohydrates than that obtained before the administration of alcohol. *In vitro*, alcohol lessens the power of the juice to digest proteids and carbohydrates, but increases that to digest fat. This is believed to be due chiefly to an action on the proferment, and the effect is more marked than that produced by enterokinase. The various ferments of the juice are therefore separate entities. The fat-splitting ferment, unlike the others, is not precipitated by alcohol; its proferment probably forms a compound with some unknown sub-

stance; this is precipitated by the alcohol and the ferment thus liberated.

W. D. H.

A New Method of Indicating Food-values. IRVING FISHER (*Amer. J. Physiol.*, 1906, 15, 417—432).—A method of indicating the amount of proteid, fat, and carbohydrate in different articles of diet by means of geometrical figures, and the methods for constructing the figures, are described in full.

W. D. H.

Formation of Glyoxylic Acid. HENRY D. DAKIN (*J. Biol. Chem.*, 1906, 1, 271—278).—Creatine and creatinine readily yield large quantities of glyoxylic acid on oxidation with hydrogen peroxide. Smaller quantities are also obtainable from glycollic acid, sarcosine, betaine, and hippuric acid. A substance giving the reactions of glyoxylic acid is readily formed by the auto-oxidation of aqueous solutions of glycine, creatine, and creatinine. Although small quantities of the acid may be isolated from blood, liver, and muscle, from urine, and from culture media in which bacteria, &c., have grown, it is not certain that it is a direct product of cell metabolism. The test proposed by Eppinger for glyoxylic acid in urine (*Abstr.*, 1905, ii, 543) is untrustworthy. The glyoxylic acid in urine probably comes from the oxidation of creatinine. Addition of hydrogen peroxide to urine gives rise to the formation of a considerable quantity of glyoxylic acid. (Compare, however, Rosenheim, *Bio-chem. J.*, 1906, 1, 233.)

W. D. H.

Rigor Mortis. J. KARPA (*Pflüger's Archiv*, 1906, 112, 199—202).—The statement is still made that the disappearance of *rigor mortis* is due to putrefaction. Bierfreund (*ibid.*, 43, 211) found, however, that the addition of antiseptics did not interfere with the phenomenon. In the present research, the muscles were treated aseptically, and the stiffening passed off in the usual way. The disappearance of *rigor mortis* is regarded as being due to autolysis. The microscopic changes in the muscular fibres are also described.

W. D. H.

NOTE BY ABTRACTOR.—The view that the passing off of *rigor mortis* is due to autolysis has been long held (compare Halliburton, *Text-book Chem. Physiol. Pathology*, 1891).—W. D. H.

Chemistry of Flesh. IV. Proteids of Beef Flesh. PERRY F. TROWBRIDGE and HARRY S. GRINDLEY (*J. Amer. Chem. Soc.*, 1906, 28, 469—505. Compare *Abstr.*, 1904, ii, 829; 1905, ii, 542; this vol., ii, 242).—The experiments described in this paper were made with lean round of beef. The total acidity of aqueous extracts calculated as lactic acid varies from 0.66 to 1.07 per cent. of the fresh meat, and is due to the presence of acid phosphates, organic acids, and proteids. The residue left after extraction with cold water is acid to litmus and phenolphthalein, but nevertheless combines with hydrochloric acid at the ordinary temperature; in one experiment, 10 grams of the air-dried residue neutralised 68.8 c.c. of *N*/10 hydrochloric acid.

Of the total proteid of raw beef, 13.56 per cent. is soluble in cold water. Of this soluble proteid, 90.04 per cent. is in a form which is coagulable by heat from a neutral solution; 8.40 per cent. exists as

albumoses, and a very small quantity as peptones; it is not supposed, however, that the albumoses and peptones are present as such in the original meat.

The coagulation of an aqueous extract of raw beef is accompanied by an increase in acidity. On the partial neutralisation of such extracts, coagulation is more complete and some of the proteid matter is precipitated. There are no well-defined degrees of temperature at which the different coagula separate; it is found that the lower the temperature at which a coagulum is separated, the longer is the time of heating required to effect complete coagulation. In the case of a cold water extract of raw beef, 11.71 per cent. is precipitated on neutralisation, 36.65 per cent. is precipitated by coagulation below 50°, 39.93 per cent. coagulates at 51—75°, and 11.71 per cent. is precipitated at 76—85°. The different fractional coagula are very similar in composition and constitution. The residue of the meat which has been extracted with cold water contains some proteids soluble in ammonium sulphate solution of 10 per cent. strength, and others insoluble. The residue left after extraction first with cold water and afterwards with ammonium sulphate solution is almost entirely soluble in $N/20$ potassium hydroxide.

E. G.

Heat of Combustion and Composition of the Bones of Guinea-pigs in Relation to their Age. J. TRIBOT (*Compt. rend.*, 1906, 142, 906—907. Compare Abstr., 1905, ii, 542).—The amount of mineral matter in the bones reaches its maximum at the 150th day, then decreases to the 555th day, after which it remains fairly constant. Similar data are given in reference to water, phosphoric acid, and the heat of combustion.

W. D. H.

Pyrimidine Bases of the Nucleic Acid obtained from Fishes' Eggs. JOHN A. MANDEL and PHOEBUS A. LEVENE (*J. Biol. Chem.*, 1906, 1, 425—426).—It is generally accepted that the unfertilised egg contains no true nuclein derivatives. Kossel failed to demonstrate the presence of purine bases in the unfertilised hen's egg. The present work was an attempt to obtain true nucleic acid from fishes' eggs by Levene's method. The substance obtained had the general properties of a true nucleic acid; it, however, resembled that obtained from plant cells by yielding only two pyrimidine bases, namely, uracil and cytosine; thymine was absent. In animal tissues and spermatozoa, the nucleic acid yields thymine usually in excess of the other two bases.

W. D. H.

Acetone Formation in the Liver. I. GUSTAV EMBDEN and F. KALBERLAH. II. GUSTAV EMBDEN, H. SALOMON, and FR. SCHMIDT (*Beitr. chem. Physiol. Path.*, 1906, 8, 121—128, 129—155).—By perfusing the "surviving" liver with normal blood, acetone is formed. This does not occur with lung, kidney, or muscle. The isolated liver is able to form acetone from various chemical substances. Of the aliphatic amino-acids, leucine also yields acetone. *iso*Hexoic acid gave negative results, whereas *isovaleric* acid gave positive results, although its amino-compound is inactive in this direction. Butyric

and β -hydroxybutyric acids yield large quantities of acetone. Aromatic substances, the ring of which is destroyed in the body (tyrosine, phenylalanine, &c.), form acetone; whilst others, the aromatic nucleus of which is not broken up (phenylacetic acid, phenylpropionic acid, &c.), do not. Conclusions of a theoretical nature are drawn as to the origin of acetone in the body in health and disease.

W. D. H.

Ion Proteid Compounds. II. Influence of Electrolytes on Staining of Tissues by Erythrosin [Tetraiodofluorescein] and Methyl-green. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1906, 1, 279—304).—In general, after treatment with electrolytes in which the anion has a greater transport number than 0.5, infusoria and gelatin plates stain deeply in methyl-green, and faintly in tetraiodofluorescein. If the transport number is less than 0.5, the opposite result is obtained. The hypothesis urged is that there are unstable ion-compounds in protoplasms, the ion of which is replaceable by other ions, the ion present in the greatest mass forming the greater part of the compound, and the acid or basic properties of the compound being determined by the acid or basic properties of the ion. On investigation, however, it was found that salts of heavy metals, acids, and alkalis were exceptions to this rule, and much of the present paper is devoted to explaining these away.

W. D. H.

Factors influencing Secretion. JOHN B. MACCALLUM (*J. Biol. Chem.*, 1906, 1, 335—344).—Three main factors in secretion are discussed, namely, (1) the blood pressure as in the kidney, (2) an activity of the gland cells similar to muscular contraction, or at least governed in many cases by the same conditions, and (3) changes in permeability of the cells.

W. D. H.

Proteolysis in Cows' Milk Preserved by means of Formaldehyde. W. G. TICE and HENRY C. SHERMAN (*J. Amer. Chem. Soc.*, 1906, 28, 189—194).—The milk was treated with formaldehyde (0.07—0.1 per cent.) within two hours after milking, and kept in tightly stoppered bottles in diffused daylight. Analyses were made within the next few days, and after intervals of 11, 17, 28, 37, and 43 months. The samples generally remained unchanged in appearance for about a year. In all cases in which bacteria were found, they were few in number and developed slowly, and it is probable that bacterial action was thoroughly suppressed.

The analytical results showed that the albumin was largely digested before the casein was appreciably reduced; subsequently, as the casein diminished, the nitrogen as albumin and syntonin changed only slightly, the increase appearing first in the proteoses and then in the peptones and amino-compounds. In the last sample, the proteoses and peptones were to a great extent broken up into amino-compounds. There was a loss of lactose (0.18—0.39 per cent.), whilst the acidity, calculated as lactic acid, varied from 0.21 to 1.43 per cent. In the case of milk treated with 0.1 per cent. of sodium fluoride, sodium salicylate, or hydrogen peroxide, Hahn and Mettler found that the

total acidity (as lactic acid) never equalled the lactose destroyed, and that no marked digestion of the casein took place before 25—30 per cent. of the lactose had disappeared. N. H. J. M.

Acidimetry of Urine. Influence of Nutrition and Muscular Work on Urinary Acidity. Influence of Nutrition on the Water of the Body. AM. VOZÁRIK (*Pflüger's Archiv*, 1906, 111, 473—496, 497—525, 526—536).—The first paper of the series is a discussion and comparison of the many methods of acidimetry used in work on the urine. In the second, the conclusions drawn are as follows: the more the nitrogenous material in the diet, the more acid the urine; in fact, the acidity is stated to be a linear function of the nitrogenous substance in the diet. If y represent the former in c.c. of decinormal acid and x the latter in grams, then it was found in experiments in one person that $y = 3.91x + 40$, and in another (the author) $y = 2.40x + 189$. There is a similar relationship between urinary acidity and the phosphoric acid of the urine. A change of diet from animal to vegetable food, or *vice versa*, causes a fall or rise in acidity respectively, lasting four or five days, followed by the reverse. Muscular work raises the acidity by 38 per cent. This is an indirect result attributed to increased katabolism.

The conclusions drawn in the third paper are that a diet rich in proteids raises the need of the body for water. The mean value of the diuresis so produced is not dependent on the amount of proteid. In the first two or three days of a proteid rich diet, the increase of water taken is mainly excreted by the kidneys; later diuresis disappears, and the excess of water is got rid of mainly by the lungs and skin.

The papers are illustrated by full analytical data. W. D. H.

The Influence of Alimentation on the Value of Urologic Coefficients. ALEXANDRE DESGREZ and J. AYRIGNAC (*Compt. rend.*, 1906, 142, 851—853).—The proportions between the different constituents of the urine, for instance, between uric acid and urea, are termed urologic coefficients. Examples are given of the variations which occur on different diets, especially vegetarian diet, milk, flesh food, &c. Theoretical conclusions are drawn from these. W. D. H.

Carbamates. JOHN J. R. MACLEOD and H. D. HASKINS (*J. Biol. Chem.*, 1906, 1, 319—334).—Solutions of ammonium carbamate in water quickly decompose until a certain equilibrium between carbamate-carbon dioxide and total carbon dioxide, and between carbamate-ammonia and total ammonia is established. Solutions of ammonium carbonate (sesquicarbonate) contain proportionately less carbamate than the above because of the acid carbonate which they contain. When kept for some time in a tightly corked flask, the carbamate does not become less, but appears slightly to increase. The addition of ammonia to solutions of ammonium carbonate or carbamate increases the amount of carbamate. The addition of small amounts of sodium carbonate to solutions of the acid carbonate increases the carbamate. The addition of excess of carbonate of course lowers the ratio of carbamate-carbon dioxide to total carbon dioxide.

The addition of sodium carbonate to liquids such as urine, which contain ammonium salts, causes carbamate to be formed in relatively large amount, therefore stale urine and citrate urine contain carbamates.

A solution of ammonium carbamate in ice-cold water depresses the freezing point of water less than does the same solution after standing a few minutes at room or body temperature. This is accounted for by the conversion of carbamate (two ions) into ammonium carbonate (three ions).

W. D. H.

Glycine and Total Mono-amino-acids in Pathological Urine.

J. WALKER HALL (*Bio-chem. J.*, 1906, 1, 241—248).—Small quantities of mono-amino-acids (including glycine, which was specially investigated) occur in normal urine. The amount is subject to considerable variation. In a case of leucæmia, and in another of rheumatoid arthritis, the amount of glycine exceeded the normal. In two cases of gout, the amount of total mono-amino-acids (estimated by Fischer and Bergell's method with β -naphthalenesulphonic chloride) varied within normal limits; the amount was, however, increased by the administration of an increase of proteid (casein) in the diet, or of glycine. Under ordinary conditions, glycine is discharged as urea. The cases examined are admittedly too few for general deductions to be drawn.

W. D. H.

Production of Methyl Mercaptan by Fæcal Bacteria in Peptone Bouillon.

CHRISTIAN A. HERTER (*J. Biol. Chem.*, 1906, 1, 421—424).—The failure experienced in finding mercaptan in the contents of the lower bowel does not exclude its formation in the upper bowel and subsequent absorption. When the mixed fæcal bacteria from healthy persons are grown in peptone broth, only a trace of mercaptan is obtained, though the amount is larger in children. In various pathological conditions (pernicious anæmia, marasmus, chronic dyspepsia, &c.) the amount is increased. An abundant production of hydrogen sulphide is usually obtained both in health and disease.

W. D. H.

Effects of Tuberculin absorbed from the Digestive Canal in Healthy and Tuberculous Animals.

A. CALMETTE and M. BRETON (*Compt. rend.*, 1906, 142, 616—618).—Tuberculin absorbed from the alimentary canal is toxic for non-tuberculous animals, and especially for young animals. No tolerance for doses given in this way was manifested towards progressively increasing doses. Tuberculous guinea-pigs are affected by doses of 1 mg., which have no effect on healthy animals. In animals suspected of tuberculous disease the diagnostic reaction with tuberculin is obtainable not only by its subcutaneous injection, but also when it is given by the digestive canal.

W. D. H.

Influence of X-Rays on Nitrogenous Metabolism and on the Blood in Myelogenous Leucæmia.

OWEN T. WILLIAMS (*Bio-chem. J.*, 1906, 1, 249—254).—The influence of X-ray treatment in a case of this disease was to increase the excretion of nitrogen in the urine, and to produce, on certain days at any rate, greater utilisation of the proteid in the diet. Uric acid was also increased. A marked increase of leucocytes in the blood coincided with

constitutional disturbances, which are attributed to disintegration products from the leucocytes. As the uric acid increases, the basophilic tendency of the granules in the leucocytes decreases. It is suggested that in X-ray treatment long intervals should be allowed between the exposures to allow of the excretion of toxic products. W. D. H.

Action of Radium on the Virus of Rabies. JEAN DANYSZ (*Ann. Inst. Pasteur*, 1906, 20, 206—208).—Tizzoni and Bongiovanni state that by the action of radium emanations on the virus of rabies *in vitro* a vaccine is obtained, and that by making the rays act on the eye or on some point in the central nervous system, it is possible to cure rabies. These statements are not confirmed. It was further found extremely difficult to obtain destruction or attenuation of the microbes of rabies in cultures by exposing them to the action of radium. W. D. H.

p-Ethoxyphenylcamphorylimide (Camphenal) as an Antipyretic. ELIJAH M. HOUGHTON (*Amer. J. Physiol.*, 1906, 15, 433—443. Compare this vol., ii, 188).—The experiments recorded show that camphenal has but little antipyretic action as compared with acetophenetidine. The drug has no value as a therapeutic agent; it is, however, interesting in showing that the camphoryl group cannot take the place of the acetyl in acetophenetidine without diminishing its antipyretic properties. W. D. H.

Administration of *l*-Alanine to a Normal Dog. ALFRED SCHITTENHELM and A. KATZENSTEIN (*Chem. Centr.*, 1906, i, 1279; from *Zeit. exp. Path. Ther.*, 2, 560—561).—After administering 20 grams of *l*-alanine to a dog which weighed 21.5 lbs., *l*-alanine was excreted. 4.7 grams of β -naphthalenesulphoalanine were obtained. E. W. W.

Toxicity of Chemical Compounds estimated by their Hæmolytic Effects. ALB. J. J. VANDEVELDE (*Chem. Zeit.*, 1906, 30, 296—297).—A large number of alcohols, ketones, acids, esters, oils, &c., was investigated. Toxicity in the series of alcohols, aldehydes, ketones, and esters increases with the number of carbon atoms. The most marked exception to this rule was found among the acids, the toxicity of formic, acetic, and propionic acids being greater than that of butyric acid; in the acids with 5 carbon atoms upwards the usual rule holds. Heptinene is eighty-two times more poisonous than ethyl alcohol. W. D. H.

Detection of Poisoning by Veronal. GUSTAV FRERICHS and HEINRICH FRERICHS (*Arch. Pharm.*, 1906, 244, 86—90).—A patient for whom kamala had been prescribed fell into a deep sleep shortly after taking the drug and died sixty-five hours later. The body was examined for veronal in the suspicion that this had been supplied by the druggist instead of kamala. By extraction with ether a considerable amount of veronal was obtained from the urine. Veronal was also isolated from the patient's stomach and part of the intestine, but

only in small quantity ; the stomach had been pumped out one and a half hours after the drug had been administered. From the liver, spleen, and kidneys, no veronal could be isolated. C. F. B.

Chemistry of Vegetable Physiology and Agriculture.

Voges and Proskauer's Reaction for Certain Bacteria.

ARTHUR HARDEN (*Proc. Roy. Soc.*, 1906, **77**, B, 424—425).—Certain bacteria grown in a medium containing dextrose and peptone show an eosin-red fluorescent colour at the open end of the tube when potassium hydroxide is added and the tube is left for twenty-four hours. This is due to acetylmethylcarbinol, formed by the action of the bacteria on the dextrose (compare Harden, this vol., ii, 381), which, in presence of potassium hydroxide and air, is oxidised to diacetyl, and then reacts with some constituent of the peptone water. E. F. A.

Influence of Calcium and Magnesium Salts on Certain Bacterial Actions. S. MACHIDA (*Bul. Imp. Centr. Agr. Exp. Stat. Japan*, 1905, **1**, 1—12).—The putrefaction of urine is retarded by calcium salts and assisted by magnesium salts. Tricalcium phosphate is utilised by some putrefying bacteria, and it is probable that in the soil the tricalcium salt is converted into an available form.

Magnesium carbonate is much more favourable to nitrification than calcium carbonate. N. H. J. M.

Bactericide Action of Sodium Phenylpropiolate. YOSHINAO KOZAI (*Bul. Imp. Centr. Agr. Exp. Stat. Japan*, 1905, **1**, 69—72).—Sodium propiolate (1 per cent.) acted strongly on *Vibrio cholerae*, *Bacillus cyanogenus*, *B. capsulatus*, *B. denitrificans*, *B. flacherie der Nonne*, *B. fluorescens liquefaciens*, *Proteus mirabilis*, and *P. vulgaris* in three hours; a great number of the bacteria is destroyed immediately by 3 per cent. solutions. Spores will, however, develop even after twenty-four hours in a 3 per cent. solution; and *B. subtilis* was not completely destroyed by a 5 per cent. solution in twenty-four hours.

A 0.04 per cent. solution of phenylpropionaldehyde was found to retard the growth of many bacteria, whilst on some it had no effect. N. H. J. M.

Chemical Action of *Bacillus lactis aërogenes* on Dextrose and Mannitol: Production of β -Butyleneglycol and Acetylmethylcarbinol. ARTHUR HARDEN and GEORGE STANLEY WALPOLE (*Proc. Roy. Soc.*, 1906, **77**, B, 399—405).—*Bacillus lactis aërogenes* grown anaerobically in a medium containing Witte-peptone and dextrose produces lactic, acetic, succinic, and formic acids, ethyl alcohol, carbon dioxide, and hydrogen. These account, however, but

for about two-thirds of the carbon of the dextrose. The neutral liquid containing the products of fermentation on evaporation and extraction with alcohol yielded an optically active oil boiling at $181-183^{\circ}$ (corr.), and having $[\alpha]_D$ from 0.46 to 0.71, which is $\beta\gamma$ -butylene glycol, $\text{OH}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{OH}$, whilst the distillate contained small quantities of acetylmethylcarbinol.

From mannitol, the same products were obtained, acetylmethylcarbinol and the glycol being produced, however, in much less quantity.

Compared with *B. coli communis* (Harden, Trans., 1901, 79, 601), *B. lactis aërogenes* produces slightly more alcohol, and the new products are formed at the expense of that part of the dextrose molecule which in the *B. coli* fermentation yields acetic and lactic acids. Both bacteria produce twice as much alcohol from mannitol as from dextrose.

E. F. A.

Gas Production by Fæcal Bacteria grown on Sugar Bouillon. CHRISTIAN A. HERTER and HERBERT C. WARD (*J. Biol. Chem.*, 1906, 1, 415—419).—The amount of gas produced in the anaërobic portions of fermentation tubes by the mixed bacteria of fæces in various sugars added to peptone bouillon was estimated; about one-tenth of the mixed gas was carbon dioxide. In certain pathological conditions, the amount of gas obtained was below the normal, namely, in cases of marasmus, diabetes, and fever. In digestive disorders and pernicious anæmia, the same is true, but great fluctuations were noticed. The explanation which is most probable is that there is an interference with the normal gas-producing properties of organisms of the *Bacillus coli* group. Such bacteria may be killed in the lower bowel, or their effects inhibited by other organisms. Differences in staining reactions of the bacteria were also noticed; an inability to take up the gram stain is associated with increased gas production.

W. D. H.

Fermentation of Sugar-cane Products. CHARLES A. BROWNE, jun. (*J. Amer. Chem. Soc.*, 1906, 28, 453—469).—The green tops of the sugar-cane contain invertase; it has been found that if these tops are removed when the cane is cut, the diffusion of the enzyme into the stalk is prevented and a smaller loss of sucrose occurs.

The rapid darkening in colour which sugar-cane juice undergoes immediately after expression is due to oxydases. If quinol is added to the fresh juice, it is rapidly oxidised and a marked absorption of oxygen takes place. The fresh juice has germicidal properties, the number of bacteria decreasing for several hours after expression; in the case of juice from sterilised canes, however, the number of bacteria increases from the commencement.

Dextran, the product of the viscous fermentation of cane juice, is probably a hydrated product of variable composition; a specimen which was examined had $[\alpha]_D + 201.8^{\circ}$ at 20° . On hydrolysis with sulphuric acid, dextrose was the only sugar which could be detected. The viscous fermentation exerts a powerful reducing action on the cane juice with formation of mannitol.

A fermentation which is of common occurrence in Louisiana results in the formation of cellulose. This fermentation, unlike the viscous, is aerobic and is believed to be due to *Bacterium xylinum*. The amount of cellulose formed in a specimen of cane juice was about 7 per cent. of the total sugar fermented.

Among other products formed in fermenting juices, mannan, chitin, and acetylmethylcarbinol have been identified.

A sample of molasses scum had the following composition: moisture, 10.00 per cent.; chitin, 11.30 per cent.; proteids, 31.62 per cent.; fat, 27.50 per cent.; ash, 5.58 per cent.; undetermined (nitrogen-free), 14.00 per cent. The fat resembled butter in composition and gave the following constants: saponification number, 223.1; iodine absorption, 28.17; Reichert-Meissl number, 30.36; m. p. 35°; m. p. of the insoluble acids, 41°; iodine number, 30.53; acid number, 85.2; ether number, 137.9; mean molecular weight of soluble acids, 129.7; mean molecular weight of insoluble acids, 283.2. E. G.

Amounts of Nitrates and Nitrites in Witte-peptone. With Special Reference to the Indole and Cholera Reaction. WILLIAM B. WHERRY (*Chem. Centr.*, 1906, ii, 1037; from *Dept. Bureau Govt. Lab. Manila*, 1905, No. 31, 17—35).—Nitrites, and probably nitrates, may occur in a variety of substances (water, peptone, and filter-paper), and show a distinct nitrite reaction with sulphanilic acid and naphthylamine. The cholera vibrio does not produce nitrites in peptone solutions free from nitrates and nitrites, prepared from dialysed Witte-peptone free from nitrites. N. H. J. M.

Chemical Processes in the Assimilation of Elementary Nitrogen by Azotobacter and Radiobacter. JULIUS STOKLASA, ADOLF E. J. TRNKA, and EUGEN VÍTEK (*Chem. Centr.*, 1906, i, 1036—1037; from *Ber. deut. bot. Ges.*, 24, 22—32).—Dextrose is better than mannitol as a source of carbon for azotobacter. One gram of the dry substance liberates in twenty-four hours approximately 1.27 grams of carbon dioxide, whilst *Bacterium Hartlebii* produces 0.6 gram, and *Clostridium gelatinosum* 0.48 gram of carbon dioxide. The decomposition products of mannitol are lactic and acetic acids, and in one case butyric acid was found. Dextrose yields lactic, acetic, and formic acids. Carbon dioxide and hydrogen are the only gases, the latter only in small quantities, being probably utilised in producing water. Hydrogen is probably of importance in the assimilation of nitrogen. N. H. J. M.

Nitrification and Ammonification of some Fertilisers. GEORGE S. FRAPS (*J. Amer. Chem. Soc.*, 1906, 28, 213—223. Compare *Abstr.*, 1905, ii, 110).—The group of organisms which produce ammonia from manures is less sensitive to the condition of plant-food than nitrifying organisms. Production of ammonia was found to be most active during the first week; in the third week it is generally negative owing to nitrification.

Nitrification begins in the second week, reaches its maximum in the third week, and then decreases. The total change is greatest during

the first week, decreases until the fourth week, after which it is somewhat irregular.

N. H. J. M.

Detection of Typhoid Bacilli in Drinking Water by Precipitation with Ferric Oxychloride. A. NIETER (*Chem. Centr.*, 1906, i, 1187; from *Hyg. Rundschau*, 16, 57—59).—The author approves of Müller's process for the detection of typhoid bacilli by precipitating the water with ferric oxychloride and examining the deposit.

L. DE K.

Removal of Dextrose from Cane and other Molasses by Fermentation. HENRI PELLET, L. PELLET, and PAIRAULT (*Chem. Centr.*, 1906, i, 947—948; from *Bull. Assoc. Chim. Sucr. Dist.*, 23, 639—647).—Experiments with a variety of yeast showed that it is possible to remove the greater part of the dextrose by fermentation.

N. H. J. M.

Amounts of Poison necessary for killing a Given Weight of Living Substance. THOMAS BOKORNY (*Chem. Centr.*, 1906, i, 1178; from *Pharm. Centr.*, 47, 121—124, 146—148, 162—165, and 188—191. Compare this vol., ii, 297).—The experiments were mostly with pressed yeast. One per cent. lactic acid kills yeast, but not 0.1 per cent. solutions. Mercuric chloride and formaldehyde act on yeast in 0.01 per cent. solutions. Mercury and silver nitrate solutions (0.001 per cent.) act on infusoria. Insect larvæ and infusoria are killed after some time by copper sulphate (1:200,000). The amounts necessary to kill 10 grams of yeast are: mercuric chloride, 0.01 gram; silver nitrate (0.01 per cent.), 0.01—0.02 gram; and copper sulphate, 0.0025—0.01 gram. The same amount of yeast is killed by 0.03 gram of chlorine and 0.05—0.02 gram of potassium permanganate, but not by 1 gram of potassium chlorate (1 per cent. solution) or by 1 gram of hydrogen peroxide. The action of butyric acid on yeast is comparable with that of hydrochloric acid. Aniline dyes rapidly kill infusoria.

N. H. J. M.

Toxicity of Sodium Chloride and its Prevention by other Salts. W. J. V. OSTERHOUT (*J. Biol. Chem.*, 1906, 1, 363—369).—Young algæ (*Vaucheria sessilis*) live for three or four weeks in distilled water, but are killed in a few minutes by 3*M*/32 sodium chloride, and in a few days by *M*/10,000 sodium chloride. The toxicity of the former solution is inhibited by adding calcium chloride in the proportion of 1 part to 100 of sodium chloride. The plants develop normally and produce mature fruit in a 3*M*/32 sodium chloride solution, to which have been added small quantities of magnesium chloride, magnesium sulphate, potassium chloride, and calcium chloride, all of which are toxic when used singly.

W. D. H.

Relationship between Chemical Constitution and Disinfecting Properties. HEINRICH BECHHOLD and PAUL EHRLICH (*Zeit. physiol. Chem.*, 1906, 47, 173—199).—The disinfecting action of numerous substances of phenolic nature has been studied, chiefly on

diphtheria bacilli, but also on other pathogenic bacteria. None of the compounds used precipitated albumin, but it was found that even the most active were of no use for internal disinfection in the animal system, as their activity is largely diminished in the presence of blood serum.

The introduction of halogen atoms into the phenol molecule increases the activity, and the increase is largely proportional to the number of atoms introduced. For example, 1 gram-molecule of pentabromophenol has the same effect on diphtheria bacilli as 500 gram-molecules of phenol. The introduction of alkyl or alkyl and halogen groups increases the activity, as does also the union of two molecules of phenol directly or by means of the following chains: CH_2 , $\text{CH}(\text{OH})$, $\text{CH}(\text{OMe})$, $\text{CH}(\text{OEt})$; whereas union by means of a carbonyl or sulphone group lessens the activity. The activity is also diminished by the introduction of carboxyl groups into the benzene nucleus.

The following are among the most active substances: Tetrabromo-*o*-cresol; for example, its action on the organisms is perceptible even in a dilution of 1 in 200,000, whereas phenol only shows an effect with a dilution of 1 in 800; the compound also possesses the valuable property of being but slightly poisonous. Tetrachloro-*o*-diphenol, the corresponding bromo-derivative, and hexabromodihydroxydiphenylcarbinol; the last, however, appears to have but little action on ordinary water bacteria.

The introduction of halogen into the phenol molecule first diminishes the poisonous properties, but afterwards acts in the opposite direction, so that trichloro- and tribromo-phenols are as poisonous as phenol, and the tetra- and penta-derivatives much more poisonous. The introduction of alkyl groups compensates to a large extent the poisonous effects of the halogen atoms.

J. J. S.

Antiseptic Properties of the Gases produced by Burning Sugar. AUGUSTE TRILLAT (*Chem. Centr.*, 1906, i, 951—952; from *Bull. Assoc. Chim. Sucr. Dist.*, 23, 655—657. Compare Abstr., 1905, ii, 325).—By burning sugar (5 grams) under a bell-jar of 10 litres capacity, broth cultures were sterilised in four hours. Similar experiments with 4 kilos. of sugar and with 6 kilos. of molasses in a space of 100 cubic metres were generally, but not always, successful. The production of formaldehyde is increased by mixing the sugar with some indifferent porous substance.

N. H. J. M.

Action of some Alkaloids on Pollen. HENRI COUPIN (*Compt. rend.*, 1906, 142, 841—843).—As an explanation of the failure of pollen to germinate completely on the stigma of flowers other than those from which it is derived, it is suggested that toxic substances may be present in the stigma and styles to which only the pollen grains of the same flower are adapted.

Experiments with the pollen of *Narcissus pseudo-Narcissus* showed that the following amounts of alkaloids are toxic: solanine, 1/23,000; veratrine, 1/21,000; strychnine, 1/12,000; morphine, 1/11,000; codeine, 1/5000; aconitine, 1/4000; caffeine, 1/3000; narcotine and cocaine, 1/2500; betaine, 1/1500; cicutine and brucine, 1/700. The toxicity

of alkaloids varies with different kinds of pollen, and the same alkaloids, when in greater dilution, may act as nutrients. The pollen of narcissus produces longer tubes in solutions of the hydrochlorides of solanine (1/30,000), veratrine (1/28,000), narcotine (1/3500), and brucine (1/3000) than in distilled water.

N. H. J. M.

Action of Carbon Dioxide on the Latent Life of some Dried Grains. PAUL BECQUEREL (*Compt. rend.*, 1906, 142, 843—845. Compare Abstr., 1905, ii, 474 and 604).—Decorticated and perforated seeds of various kinds which had been immersed in water for a quarter of an hour were all killed by being kept in an atmosphere of carbon dioxide for eleven months. Similar seeds in their naturally dry condition after being kept a year were only injured in a few cases; whilst others, which had been dried in a vacuum over baryta at 45°, all germinated after eleven months in carbon dioxide.

N. H. J. M.

Assimilation of Potassium and Sodium by Plants. THEODOR PFEIFFER, ALBERT EINECKE, W. SCHNEIDER, and A. HIEPER (*Chem. Centr.*, 1906, i, 1182; from *Mitt. landw. Inst. Univ. Breslau*, 3, 567—613).—The experiments were made with barley grown in soil free from zeolites, to which various double silicates free from potassium were added. Addition of potassium manure (300 mg. K_2O) resulted in an increase of 27 grams, whilst 1 gram K_2O produced 22.14 grams of starch.

Sodium acts indirectly by liberating potassium from the soil. It cannot be said that sodium has no direct action in seed production by taking the place of potassium, but the action, if it takes place at all, is too slight to be of importance.

N. H. J. M.

Variations in the Nitrogen and Phosphoric Acid of the Sap of an Oleaginous Plant. GUSTAVE ANDRÉ (*Compt. rend.*, 1906, 142, 902—904. Compare this vol., ii, 192).—The total nitrogen, nitrogen as nitrates, and phosphoric acid were determined in *Mesembrianthemum crystallinum* at five periods of growth from May 31st to October 4th.

N. H. J. M.

Studies on the Banana. I. E. MONROE BAILEY (*J. Biol. Chem.*, 1906, 1, 355—361).—The experiments described indicate that ripening (formation of soluble carbohydrates and decrease of total carbohydrates) proceeds slowly, if at all, when the gaseous exchange in the banana is prevented by some inert coating.

W. D. H.

Formation and Distribution of Terpenic Compounds in *Citrus aurantium*. EUGÈNE CHARABOT and G. LALOUÉ (*Compt. rend.*, 1906, 142, 798—801. Compare Abstr., 1904, ii, 634, and 1905, ii, 112).—In May, the leaves of *Citrus aurantium* contained a higher percentage of odoriferous substances than the stems; the absolute quantity was about twelve times as much as in the stems. In June (about three weeks later), the percentage of essence increased considerably in the leaves and diminished in the stems.

The amount of citral in the essence is only small and is chiefly in the leaves. Between the first and second stages of growth there is an increase in the amount of citral in the essence and an increase in the relation between the combined and total alcohol and a decrease in total alcohol.

N. H. J. M.

Seeds and Oil of *Morynga pterygosperma*. LEOPOLD VAN ITALLIE and C. H. NIEUWLAND (*Arch. Pharm.*, 1906, 244, 159—160. Compare Lewkowitsch, *Abstr.*, 1904, ii, 218).—The husks form 30 per cent. of the seeds. From the kernels, light petroleum extracts 36 per cent. of a fatty oil. The residue contains: water, 6.1; nitrogen, 9.4; cellulose, 5.4; ash, 5.5 per cent.

The oil of ben had the sp. gr. 0.912 at 15°; acid number, 13.5; saponification number, 187; iodine number, 72; Reichert-Meissl number, 0.49; Hehner's number, 95 (the acids not soluble in water contained 71 per cent. of oleic acid, which had iodine number 86 and refractometer number 1.4586 at 25°, and yielded dihydroxystearic acid on oxidation).

At 10—12°, a solid portion separates from the oil; the residual liquid had sp. gr. 0.913 at 15°; acid number, 9.9; saponification number, 187.

The phytosterol obtained from the oil melted at 134—135°.

C. F. B.

Fat of the Palm Fruit of Surinam. J. SACK (*Chem. Centr.*, 1906, i, 1106; from *Inspect. Landbouw. West-Ind. Bul.*, 5, 9—11).—The kernels of *Acrocomia sclerocarpa* may contain as much as 24.8 per cent. of fat, consisting of the glycerides of oleic and lauric acids. The kernels of *Bactris Plumeriana* contain 34.8 per cent. of fat melting at 32°, a mixture of triolein (13.6) and trilaurin (86.4 per cent.).

N. H. J. M.

Wax of the Bark of *Jatropha curcas*. J. SACK (*Chem. Centr.*, 1906, i, 1106; from *Inspect. Landbouw. West-Ind. Bul.*, 5, 8—9).—The wax is a mixture of myricyl alcohol and myricyl melissate.

N. H. J. M.

Detection of Glucosides in Plants by means of Emulsin. ÉMILE BOURQUELOT (*J. Pharm. Chim.*, 1906, [vi], 23, 369—375).—The application of the method already described (*Abstr.*, 1902, ii, 55) has resulted in the discovery of glucosides, capable of being hydrolysed by emulsin, in several plants enumerated in the original. The leaves of *Ligustrum japonicum* appear to contain syringin, whilst the branches of *Jasminum nudiflorum* and the leaves of *Viburnum tinus* probably contain glucosides hitherto undescribed. A new glucoside, *taxicatin*, has been isolated from the leaves of the yew (*Taxus baccata*).

T. A. H.

Products containing Tannin. J. SACK (*Chem. Centr.*, 1906, i, 1106—1107; from *Inspect. Landbouw. West-Ind. Bul.*, 5, 1—8).—The dry matter of the bark of *Rhizophora mangle* contains up to 24.5

per cent. of tannin. *Lecythis amara* contains only small amounts of tannin, and in addition a white substance resembling saponin. The bark of *Bigonia inaequalis* and *Carapa guyanensis* yielded 14 and 5 per cent. of tannin respectively. N. H. J. M.

Ricinus Residues. A. HALENKE and M. KLING (*Landw. Versuchs-Stat.*, 1906, 64, 51—86).—A résumé of analyses of ricinus seeds and residues with references to the original papers. N. H. J. M.

Analysis of Raspberry Juice. RUDOLF HEFELMANN, PAUL MAUZ, and F. MÜLLER (*Zeit. öffentl. Chem.*, 1906, 12, 141—155).—The following results were obtained on the analysis of fifty samples of raspberry juice pressed from fruit grown in the year 1905: total solids, 2.89 to 4.94, average 4.09 per cent.; ash, 0.312 to 0.505, average 0.430 per cent.; alkalinity of ash, 4.50 to 6.90, average 5.61 c.c. of N/1 acid. These results agree with the averages found in other years. W. P. S.

The Acids occurring in Raspberry Juice. R. KAYSER (*Zeit. öffentl. Chem.*, 1906, 12, 155—156).—The following acids were found in a sample of raspberry juice: tartaric acid, 0.180 per cent.; citric acid, 0.655 per cent.; malic acid (difference), 0.300 per cent.; and volatile acid (calculated as acetic), 0.045 per cent. W. P. S.

Treatment of Seeds with Copper Solutions. EMILE BRÉAL (*Compt. rend.*, 1906, 142, 904—906).—The solution was prepared by boiling starch (30 grams) in 1 litre of 0.3 per cent. copper sulphate solution. Seeds are left for twenty hours in the cold solution, superficially dried by exposure to air, immersed in lime water, and again air dried. There is no change in the appearance of the seeds, but they increase about 5 per cent. in weight.

It was found that the above treatment not only prevents cryptogamic disease, but also favours germination and increases the crop. N. H. J. M.

Physiological Action of Copper-lime Mixture on Plants. RICHARD EWERT (*Chem. Centr.*, 1906, i, 944—945; from *Ber. deut. bot. Ges.*, 23, 480—485).—Copper in the form of 1 per cent. Bordeaux mixture and 1 per cent. acetate solution was very effective in the case of currants attacked by *Gloeosporium ribis*. It seems probable that the penetration of copper into the plant may be due to substances diffusing from the leaves; solution of copper by rain could not be detected. N. H. J. M.

Correction of a Very Unfavourable Ratio of Lime to Magnesia in a Soil for the Culture of Barley. G. DAIKUHARA (*Bul. Imp. Centr. Agr. Exp. Stat. Japan*, 1905, 1, 13—16).—Pot experiments in which barley was grown in well-manured soil having the very unfavourable ratio $\text{CaO/MgO} = 0.34/1$ showed that the yield was doubled when precipitated calcium carbonate was added so as to make the ratio = 1/1. N. H. J. M.

Retention of the Injurious Nitrogen Compounds of Sugar Beet by the Sap. Stability of these Substances in the Purification Process and their Increase during Prolonged Storage of the Roots. KARL ANDRLÍK and J. URBAN (*Zeit. Zuckerind. Böhm.*, 1906, 30, 282—286. Compare Abstr., 1905, ii, 617).—In the diffusion process, about 90 per cent. of the injurious substances appears in the sap.

The relative amount of injurious matters increases when roots are stored owing to loss of sugar by respiration, and there is possibly an actual increase due to the breaking down of proteids.

Results obtained with diffusion sap gave higher numbers than the roots, and there seems to be no appreciable loss by decomposition of injurious nitrogen compounds during the manufacturing process.

N. H. J. M.

Application of Magnesia in the Form of Magnesium Sulphate for the Needs of the Rice Plant. G. DAIKUHARA (*Bul. Imp. Centr. Agr. Exp. Stat. Japan*, 1906, 1, 23—29).—In presence of calcium carbonate, the necessary amount of magnesium when applied as sulphate to paddy rice in sand culture is very small, the best ratio being $\text{CaO/MgO} = 30/1$. When both calcium and magnesium are present as carbonates, the ratio should be 1/1 (compare Asō, Abstr., 1904, ii, 765) in the case of sandy soils. In clayey soils, the best ratio will differ when the magnesium is present as sulphate.

N. H. J. M.

Stimulating Action of Potassium Iodide on Sesamum and Spinach. S. UCHIYAMA (*Bul. Imp. Centr. Agr. Exp. Stat. Japan*, 1906, 1, 35—37. Compare Suzuki, Abstr., 1903, ii, 173).—Small amounts of potassium iodide increased the yield both of sesamum and spinach. In pot experiments with sesamum there was an increase of 16 per cent. when the iodide was added at the rate of 124 grams per hectare and 25 per cent. with ten times that quantity. In a field experiment on a plot having an area of 59.5 sq. metres, the yield was increased by 24 per cent. by 25 grams of potassium iodide.

The results are practically of interest, as it is usual, along the coast, to employ sea-weed as manure.

N. H. J. M.

Lime Factor for the Tobacco Plant. G. DAIKUHARA (*Bul. Imp. Centr. Agr. Exp. Stat. Japan*, 1905, 1, 17—22).—Analysis of the ash of Virginia, Kentucky, Hungarian, and German tobacco showed that the ratio $\text{CaO/MgO} = 3.63/1, 3.78/1, 4.44/1$, and $4.11/1$ respectively, the mean being $3.96/1$.

The results of pot experiments with tobacco grown in a soil having a ratio $\text{CaO/MgO} = 1/1$, and in the same soil to which air-slaked lime had been added in such quantity as to make the ratio $= 2/1$ and $4/1$, showed that liming was beneficial. The best relation of lime to magnesia remains, however, to be ascertained in the case of tobacco.

N. H. J. M.

Analyses of Natural Humus. E. MICHELET and JOHN SEBELIEN (*Chem. Zeit.*, 1906, 30, 356—358).—The substances analysed were as

follows : (1) decayed fir wood, (2) decayed oak, (3) dark brown sludge derived from vegetation and from excrement of fresh water animals, (4, 5, and 6) light grey peat of partly animal and partly vegetable origin, (7) humus sandy soil from Aas, (8) black sandy forest soil, (9) sandy loam from Lauchstädt, and (10) Russian black soil. The results are percentages in dry matter.

	C.	H.	N.	Furfuroids.	Methyl-furfuroids.	Methoxyl number.	Loss on ignition.	Ash.
1.	52.19	5.02	0.49	3.42	3.61	3.49	98.62	1.38
2.	48.31	3.64	1.66	4.22	2.40	2.96	95.11	4.89
3.	58.14	6.87	2.93	7.49	1.45	1.33	95.56	4.44
4.	6.09	0.99	0.55	0.45	0.23	0.04	13.80	86.20
5.	6.69	0.95	0.59	0.54	0.23	0.04	14.87	85.13
6.	4.88	0.76	0.39	0.36	0.17	0.06	9.79	90.21
7.	9.21	1.40	0.74	0.70	0.32	0.12	18.47	81.53
8.	5.60	0.63	0.32	0.10	0.16	0.04	9.28	90.72
9.	1.94	0.40	0.15	0.09	0.12	0.03	5.01	94.99
10.	6.11	0.94	0.53	0.36	0.23	0.05	13.63	86.37

Fir and oak wood were found to contain respectively 10.03 and 20.18 per cent. of furfuroids and 4.70 and 5.55 per cent. of methyl-furfuroids, so that in the process of decay the furfuroids seem to be the more readily attacked. The decayed fir, the black soil from Telemarken (8), and the Lauchstädt soil contain more methyl-furfuroids than furfuroids.

N. H. J. M.

Improvement of a Soil Relatively Deficient in Magnesia. TEIKICHI NAKAMURA (*Bul. Imp. Centr. Agr. Exp. Stat. Japan*, 1906, 1, 30—34).—The soil consists chiefly of hydrous silicates and contains 1.76 per cent. of lime (chiefly as silicate) and 0.11 per cent. of magnesia.

In experiments with barley with addition of different amounts of magnesium sulphate, it was found that the best results were obtained when the ratio $\text{CaO/MgO} = 7/1$. As, for cereals generally, the best ratio is 1/1 when both are present as carbonate, the results indicate that the relative values of magnesium sulphate and magnesite are about 23 : 100.

N. H. J. M.

Analytical Chemistry.

New Method for Stating Analytical Results. GUSTAVE BRUHNS (*Zeit. anal. Chem.*, 1906, 45, 204—216).—A lengthy reply to Petersen (compare this vol., ii, 194).
L. DE K.

Sodium Carbonate and Sodium Oxalate for Standardising Purposes. SÖREN P. L. SÖRENSEN and A. C. ANDERSEN (*Zeit. anal. Chem.*, 1906, 45, 217—231).—A controversy with Lunge. The authors still prefer using sodium oxalate for the standardisation of acids. They further state that methyl-orange is a very suitable indi-

cator for technical purposes, but for delicate work phenolphthalein is to be preferred (compare Abstr., 1903, ii, 684, 750 ; 1905, ii, 415).

L. DE K.

New Form of Absorption Tube. EDGAR P. PERMAN (*Chem. News*, 1906, 93, 213).—The apparatus consists of an elongated horizontal bulb fitted at each end with a vertical bulb-tube. The absorbent just closes the orifice of the exit tube. The latter may be connected with a guard tube containing glass beads moistened with the absorbent. By using this tube all danger of regurgitation is avoided. L. DE K.

Detection of Fluorine in Alimentary Substances. JULES VILLE and EUGÈNE DERRIEN (*Bull. Soc. chim.*, 1906, [iii], 35, 239—246).—The method is based on the change in the absorption spectrum induced by adding fluorine compounds to solutions of methæmoglobin (Abstr., 1905, i, 399, 500, 622, and ii, 402). Directions are given (1) for the preparation of a standard solution of methæmoglobin and (2) for the preparation from various alimentary substances (wine, beer, milk, meat, butter, and fat) of limpid, colourless extracts containing all the fluorine compounds which may have been present in the crude substances. In any particular case, a known quantity of the methæmoglobin solution is added to the clear extract and the mixture examined spectroscopically, when, if fluorine is present, the characteristic absorption bands of the fluorine compound of methæmoglobin will be seen. T. A. H.

[Reagents for Ozone.] CARL ARNOLD (*Ber.*, 1906, 39, 1528—1529. Compare Arnold and Menzel, Abstr., 1902, ii, 352; Fischer and Braehmar, this vol., ii, 224).—As the name "tetra-base" has been used for some years for tetramethyl-*p*-phenylenediamine (Wurster, Abstr., 1888, 627), the author proposes to term tetramethyldi-*p*-aminophenylmethane, "tetramethyl-base" or "Arnold's reagent."

G. Y.

Apparatus for the Estimation of Sulphur and Carbon with Single or Double Receiver. ARTHUR WILHELMI (*Chem. Centr.*, 1906, i, 1286—1287; from *Zeit. chem. Apparatenkunde*, 1, 155—156).—An improved apparatus, the chief advantage of which is that the acid fumes are readily condensed and also that it need not be completely disconnected after each analysis. For details, the drawings in the original paper should be consulted. L. DE K.

Modified Evolution Method for the Estimation of Sulphur in Pig-iron. J. MCFARLANE and A. W. GREGORY (*Chem. News*, 1906, 93, 201).—When pig-iron is dissolved in hydrochloric acid, a not inconsiderable portion of the sulphur may escape conversion into hydrogen sulphide. The authors, therefore, have modified the original method and operate as follows.

Five grams of the powdered sample are intimately mixed with 0.5 gram of potassium hydrogen tartrate; the mixture is wrapped in filter paper, placed in a covered crucible, and heated to bright redness for

fifteen minutes. The mass will now give up all its sulphur as hydrogen sulphide when treated with dilute hydrochloric acid (2 : 1) in the usual apparatus.

L. DE K.

Estimation of Sulphur in Pyrites. C. R. GYZANDER (*Chem. News*, 1906, 93, 213—214).—0.2 gram of the finely-powdered ore is dissolved in 20 c.c. of a mixture of nitric and hydrochloric acids (3 : 1). The liquid is evaporated to dryness on the water-bath and any nitric acid is expelled by a second evaporation with 5 c.c. of hydrochloric acid. The residue is taken up with 100 c.c. of water and 1 c.c. of hydrochloric acid and the iron is reduced to the ferrous state by adding 3 c.c. of a 6 per cent. solution of hydroxylamine hydrochloride. After heating the filtrate to near boiling, the sulphuric acid is precipitated as usual with barium chloride. The precipitate is free from iron.

L. DE K.

Improved Apparatus for Estimating Total Sulphur in Coal Gas; Modification of Dreschmidt's Method. EVERHARD P. HARDING (*J. Amer. Chem. Soc.*, 1906, 28, 537—541).—About two feet in all of the gas are burnt in a specially constructed bunsen burner, the burning taking place in a space containing bromine vapour. The products of combustion are aspirated by means of a current of purified air through a 5 per cent. solution of potassium carbonate and the resulting sulphate is estimated as usual.

For details of the operation and the full description of the somewhat complicated apparatus the original article should be consulted.

L. DE K.

Estimation of Total Sulphur in Illuminating Gas. CHARLES D. JENKINS (*J. Amer. Chem. Soc.*, 1906, 28, 542—544).—About one cubic foot of the gas is burnt at the rate of 0.6 cubic foot per hour in an ammoniacal atmosphere and the condensed liquid is fully oxidised with bromine water. The resulting sulphate is then estimated volumetrically by means of the well-known barium chromate method.

A description and illustration is given of a convenient portable apparatus.

L. DE K.

Estimation of Small Quantities of Ammonia in Presence of Urea. FRENKEL (*Bull. Soc. chim.*, 1906, [iii], 35, 250—251).—A crystallising dish, 120 mm. in diameter and 45 mm. high, with ground edges, is surmounted by a spherical funnel also having ground edges. The joint is made tight by means of lard. The opening of the stem of the funnel is closed by a rubber stopper carrying (1) a tube leading to two wash-bottles in series containing a solution of potash and sulphuric acid respectively, and (2) a tube passing to the bottom of a small flask connected to a water-pump and containing a known quantity of *N*/10 sulphuric acid. In the crystallising dish is placed 25 c.c. of the solution to be examined, which must contain not more than one gram of ammonia per litre: to this is added 25 c.c. of milk of lime. A current of air is drawn through the whole apparatus by means of the water-

pump, so that the ammonia liberated is carried into the acid. At the end of two hours, the action is complete and the acid may be titrated.

T. A. H.

Estimation of Ammonia in Used Lime Liquors. HENRY R. PROCTER and DOUGLAS McCANDLISH (*J. Soc. Chem. Ind.*, 1906, 25, 254—256).—The sample is mixed with a few drops of turpentine to prevent frothing, and heated to 90° in a specially constructed apparatus. A current of air free from ammonia is drawn through by means of a water-jet pump, and the ammonia thus removed from the liquid is absorbed, as usual, in standard acid. The ammonia is completely expelled after one hour.

The ammonia affords a standard by which the activity of the liquor may be judged.

L. DE K.

Oxidation of Nitrous Acid by Hydrogen Peroxide; Estimation of Nitrates in the Presence of Nitrites. MAX BUSCH (*Ber.*, 1906, 39, 1401—1403).—The substance, containing 0.1—0.2 gram of nitrite, is dissolved in 50 c.c. of water, and, after the addition of 20 c.c. of a neutral 3 per cent. solution of hydrogen peroxide, is warmed to 70°; 20 c.c. of 2 per cent. sulphuric acid are then added. The liquid is heated to boiling and the nitric acid precipitated by the addition of 12 c.c. of a solution of "nitron" acetate (*Abstr.*, 1905, ii, 282). Nitrites in the presence of nitrates are first estimated by the permanganate method, then the total nitrate, after oxidation with hydrogen peroxide, is estimated as above.

The method is applicable to the estimation of nitrogen in nitrated cellulose. When the latter is boiled with alkali and hydrogen peroxide, the formation of ammonia is avoided (compare Häussermann, *Ber.*, 1903, 36, 3956) and the nitrogen is all present as nitrite and nitrate. The solution is acidified and the total nitrate estimated as above.

C. S.

Detection of Small Amounts of Yellow Phosphorus. RUDOLF SCHENCK and E. SCHARFF (*Ber.*, 1906, 39, 1522—1528. Compare Schenck, Mihr, and Banthien, this vol., ii, 326; Mai and Schaffer, *Abstr.*, 1903, ii, 363; Vignon, *Abstr.*, 1905, ii, 479).—The presence of small amounts, down to 0.004 mg., of yellow phosphorus in phosphorus trisulphide can be detected by the increase in the rate of discharge of an electroscope when subjected to the action of air in which the sample has been slowly oxidised at 35—55°. As no phosphorus trioxide is formed by the slow oxidation of the trisulphide, the latter alone has no effect on the conductivity of air. A convenient apparatus for carrying out the test is described and figured.

G. Y.

Estimation of Phosphoric Acid by the Citrate Method. VINCENT SCHENKE (*Landw. Versuchs-Stat.*, 1906, 64, 87—91. Compare *Abstr.*, 1905, ii, 479).—A reply to Mach (this vol., ii, 50). It is found that when very small amounts of phosphoric acid are present no precipitate is obtained when the method of the German

Association is employed, whilst the author's modified citrate method gives concordant results. The negative results are attributed to the increased solubility of the magnesium ammonium phosphate in the larger amount of ammonium citrate solution. N. H. J. M.

Estimation of the Sodium Phosphates. C. CHESTER AHLUM (*J. Amer. Chem. Soc.*, 1906, 28, 533—537).—A mixture of disodium hydrogen phosphate and trisodium phosphate may be analysed as follows: 1st Method.—Two grams of the compound are dissolved in water, and carbon dioxide is passed through for about fifteen minutes. The solution is evaporated to dryness, and by means of the Schrötter apparatus the carbon dioxide absorbed is estimated. Its weight multiplied by 7.4545 represents the trisodium phosphate. One gram of the mixed salts is dissolved in water and titrated with *N*/10 hydrochloric acid, using methyl-orange as indicator. From the number of c.c. of acid used is deducted the number of c.c. required by the trisodium phosphate (grams of same divided by 0.0164), and the difference then represents the disodium hydrogen phosphate (1 c.c. = 0.0142 gram). 2nd Method.—0.5 gram of the mixture is dissolved in 50 c.c. of water and titrated with *N*/10 acid. One gram is dissolved in 50 c.c. of water, a drop of methyl-orange is added, and then a slight excess of hydrochloric acid. After boiling, an excess of sodium carbonate is added, and the whole is evaporated to dryness in a weighed dish. Exactly one-half of the powdered residue is then tested in the Schrötter apparatus, whilst the other half is titrated with *N*/10 acid. This gives all the data necessary for calculation. The test analyses are fairly satisfactory. L. DE K.

Estimation of Arsenic by Marsh's Method. GABRIEL BERTRAND and ZOLTÁN DE VÁMOSSY (*Ann. Chim. phys.*, 1906, [viii], 7, 523—536).—A slight modification of Bertrand's process. The solution containing about 0.01 gram of arsenic is introduced gradually into the generating flask containing zinc and dilute sulphuric acid, and the hydrogen after being dried over dehydrated cotton-wool is passed through a red-hot combustion tube, 40 cm. in length. The arsenic liberated is then collected in a tube having an interior diameter of 2 mm. The hydrogen is passed through a solution of silver nitrate to retain traces of arsenic hydride which have escaped decomposition. Should any precipitate form, the liquid is acidified with nitric acid and evaporated to dryness. The residue is taken up with a little water and the silver cautiously precipitated with sodium chloride. The filtrate is evaporated with addition of sulphuric acid and the residue introduced at once into the generating flask.

The tube containing the arsenic is weighed with due precautions, rinsed with sodium hypochlorite solution to dissolve the arsenical deposit (nitric acid should not be used), dried, and reweighed.

L. DE K.

Use of Copper as an Accelerator in Marsh's Apparatus ARMAND GAUTIER (*Bull. Soc. chim.*, 1906, [iii], 35, 207—208. Compare Abstr., 1903, ii, 102).—It is pointed out that the different results

obtained by de Vámosy (this vol., ii, 196) and the author (*Ann. Chim. phys.*, 1876, [v], 8, 401) in using copper as an accelerator are probably due to the different conditions under which the two sets of experiments were made. The conclusion that platinum is a better accelerator than copper had already been arrived at by the author.

T. A. H.

Purification of Zinc and Hydrochloric Acid from Arsenic. LEONARD T. THORNE and ERNEST H. JEFFERS (*Analyst*, 1906, 31, 101—103).—The best conditions for purifying zinc by means of sodium, as originally proposed by Hehner (*Abstr.*, 1902, ii, 501), are given. The zinc is just fused in a crucible and the sodium added in small pieces at a time, employing about 1 gram for each pound of zinc. The molten metal is then poured into a second heated crucible and back again to ensure thorough mixing. The crucible is now covered and heated to dull redness, when the lid is removed and the heating continued for one hour. After being allowed to cool slightly, the crust is pierced and the molten metal poured into another hot crucible, in which it is again heated and skimmed if necessary. The zinc is finally granulated just before the solidifying point is reached.

Arsenic may be completely removed from hydrochloric acid by treating each litre of diluted acid of sp. gr. 1.1 with 2 or 3 grams of copper-tin couple, heating the mixture to boiling for about fifteen minutes, and then distilling from a small quantity of the couple, a piece of 100-mesh copper gauze being also placed in the distillation flask. The copper-tin couple may be prepared as follows: cuprous chloride is dissolved in excess of hydrochloric acid and a small quantity of tin added. Zinc dust is then added, and this reduces the remainder of the copper, together with the tin, in the form of a dark grey, spongy couple, which is washed by decantation. If the couple be nearly black in colour, too much copper is present. The residue in the distillation flask serves conveniently for the preparation of fresh couple.

W. P. S.

Estimation of Arsenic, Antimony, and Sulphur in Ores by Heating in a Current of Chlorine or of Carbon Dioxide charged with Bromine. ERNST SCHÄFER (*Zeit. anal. Chem.*, 1906, 45, 145—174).—A lengthy paper unsuitable for adequate abstraction.

The conclusion arrived at is that the decomposition in a current of chlorine is preferable to the heating in a current of carbon dioxide charged with bromine vapour (Jannasch's process).

The old process has been modified in so far that the chlorine is generated in a Kipp apparatus from compressed bleaching powder. The mineral is contained in a boat placed inside a small combustion tube.

L. DE K.

Approximate Estimation of Boric Acid. CECIL H. CRIBB and FRANCIS W. F. ARNAUD (*Analyst*, 1906, 31, 147—149).—A sensitive turmeric paper is prepared by dipping strips of blotting paper in a hot alcoholic solution containing 2 per cent. each of turmeric and tartaric acid. The strips are dried, and will detect as little as

0.0025 per cent. of boric acid when employed in the usual way. In estimating boric acid in milk, 5 c.c. of the latter are treated with 1 c.c. of *N*/1 alkali, the mixture is evaporated to dryness, ignited, the ash dissolved in 1 c.c. of *N*/1 acid, and the volume diluted to 10, 20, or 30 c.c. or more with 2 per cent. hydrochloric acid. A strip of the sensitive turmeric paper is then dipped in the solution and dried at a moderate temperature, preferably in the dark. If a pink coloration is obtained, the solution is still further diluted and again tested until the paper fails to give a reaction. The sensitiveness of the paper having been determined previously with known quantities of boric acid, a simple calculation will give the amount of boric acid in the sample of milk. The process is conducted on precisely similar lines in the case of butter and cream.

W. P. S.

Improvements in Gas Analysis. Estimation of Small Quantities of Carbon Monoxide. ROMUALD NOWICKI (*Chem. Centr.*, 1906, i, 1186—1187; from *Oesterr. Zeit. Berg. Hütt.*, 54, 6—11).—The air is first purified by means of potassium hydroxide, calcium chloride, and soda-lime, and the carbon monoxide is then oxidised by means of iodic anhydride. The action takes place at 45° and is completed at 88°. The carbon dioxide formed is then estimated as usual, or the amount of iodine liberated may be estimated as a check (compare *Abstr.*, 1905, ii, 760).

L. DE K.

Assay of Official Potassium Bromide. H. CORMIMBŒUF (*Ann. Chim. anal.*, 1906, 11, 131—134).—The chief impurity of potassium bromide is potassium chloride. In the absence of other impurities, the amount of chloride may be ascertained with sufficient accuracy by converting two grams of the heated sample into the corresponding silver compound, and then referring to a table calculated by the author.

L. DE K.

Estimation of Small Quantities of Sodium Sulphate in Magnesium Sulphate. GUSTAV MOSSLER (*Chem. Centr.*, 1906, i, 1115—1116; from *Zeit. Oesterr. Apoth. Ver.*, 44, 53—54).—12.5 grams of the suspected sample are dissolved in 40 c.c. of water and 125 c.c. of ammonium carbonate solution are added (230 grams of the official salt, 360 c.c. of ammonia of sp. gr. 0.960, water up to 1 litre). Water is added until the volume is about 246 c.c., and after standing for twelve hours the volume is made up to 250 c.c. Two hundred c.c. of the filtrate are then evaporated to dryness in a weighed platinum dish and the residue is ignited and weighed. It consists of sodium sulphate plus a constant amount (0.029 gram) of magnesium sulphate.

L. DE K.

Estimation of Silver in Alloys in the Wet Way. F. ALTNÉDER (*Metallurgie*, 1906, 3, 292—293).—One gram of the alloy is dissolved in 10 c.c. of nitric acid of sp. gr. 1.4, boiled to remove nitrous fumes, cooled, and 50 c.c. of water, 10 c.c. of nitric acid, and a few c.c. of starch solution added. The solution is then titrated with a standard solution of potassium iodide, which precipitates the silver as silver

iodide. The end of the reaction is indicated by the formation of starch iodide owing to the decomposition of the excess of potassium iodide by the nitric acid.

C. H. D.

Estimation of Calcium in Soil. D. J. HISSINK (*Chem. Centr.*, 1906, i, 961; from *Chem. Weekblad*, 3, 73—78).—Neubauer's method (this vol., ii, 52) is recommended.

N. H. J. M.

Schlagdenhauffen's Reaction [Detection of Magnesium]. J. BELLIER (*J. Pharm. Chim.*, 1906, [vi], 23, 378—381).—The author confirms Grimbert's observation (this vol., ii, 307) that Schlagdenhauffen's reagent is unstable and not very delicate. He finds the following modification more sensitive than that suggested by Grimbert (*loc. cit.*). To 10 c.c. of the magnesium solution, 1 c.c. of a one per cent. solution of potassium iodide, saturated with iodine, is added and then a solution of sodium hydroxide, drop by drop. With a solution containing 0.1 gram of magnesium per litre, a reddish-brown precipitate is formed, and a solution half as strong gives a deep reddish-brown coloration. The reaction is unsuitable for quantitative application owing to the considerable solubility in water of the precipitate formed. The product precipitated in this reaction may be obtained in quantity by mixing powdered iodine with moistened magnesia and setting the mixture aside for twenty-four hours. Attempts to determine its composition gave discordant results, and the author is of opinion that it may be merely magnesia coloured by iodine, the latter serving to render the precipitated magnesia visible.

T. A. H.

Titration of Zinc with Potassium Ferrocyanide. ERNST MURMANN (*Zeit. anal. Chem.*, 1906, 45, 174—181).—An improved method of titrating zinc with ferrocyanide. The solution, freed from interfering metals, as usual, is diluted to 100—150 c.c. and 2—5 c.c. of a 1 per cent. solution of uranyl chloride are added. The liquid should not contain more than 5—10 c.c. of free hydrochloric acid of sp. gr. 1.075. After heating to boiling, standard potassium ferrocyanide (43.11 grams of the salt per litre) is slowly run in until the liquid turns brown; a few more c.c. are then added, and the liquid is titrated back with corresponding zinc solution until the brown colour vanishes and changes to a greenish-blue (due to a trace of iron).

L. DE K.

Estimation of Small Quantities of Copper in [Drinking] Waters. EARLE B. PHELPS (*J. Amer. Chem. Soc.*, 1906, 28, 368—372).—One litre of water (or less if the amount of copper is likely to exceed 1 mg.) is evaporated to 75 c.c. and 2 c.c. of dilute sulphuric acid (1:1) are added. The liquid is then submitted to electrolysis, the cathode consisting of a stout platinum wire 50 cm. long, 40 cm. of which are coiled into a flat spiral. When the copper has deposited, the wire is at once plunged into boiling dilute nitric acid (1:3) and the liquid is evaporated to dryness. The residue is then dissolved in 100 c.c. of water, and 10 c.c. of a mixture of equal parts of hydrogen sulphide, water, and 10 per cent. potassium hydroxide are

added. The resulting coloration, which is fairly permanent, is matched, as usual, by means of a copper sulphate solution of known strength

L. DE K

Estimation of Manganese in Iron and Steels. OMER BRICHANT (*Ann. Chim. anal.*, 1906, 11, 124—127).—One gram of iron or steel is dissolved in 25 c.c. of nitric acid of sp. gr. 1.135. After expelling nitric fumes, water is added to reduce the temperature to about 50°, and after filtering, if necessary, 10 c.c. of *N*/10 silver nitrate and 0.2 gram of ammonium persulphate are added, and the whole is then heated until the rose coloration has disappeared with or without separation of manganese dioxide. After completely decolorising the liquid with ferrous sulphate, the solution is allowed to cool to 60°, when another 0.2 gram of persulphate is added. After ten minutes, the whole of the manganese will be in the state of permanganate, and when cold this may be titrated with a standard solution of sodium arsenite (0.9 gram of arsenic trioxide and 3 grams of sodium hydrogen carbonate in 1 litre).

In the case of Spiegeleisen or ferromanganese, 1 gram of the sample is dissolved in a sufficiency of nitric acid and the solution is diluted to 250 c.c.; 25 c.c. (0.1 gram) are then mixed with 25 c.c. of nitric acid and treated with silver nitrate and persulphate as already directed.

L. DE K.

Estimation of Small Quantities of Nickel in Organic Substances. H. W. ARMIT and ARTHUR HARDEN (*Proc. Roy. Soc.*, 1906, 77, B, 420—423).—The substance is incinerated with care in a porcelain crucible and the ash treated with hydrochloric acid, evaporated to dryness, and taken up with dilute acid. Iron and phosphates are removed by precipitation with excess of ammonia, the precipitate being dissolved in dilute acid and again precipitated once or twice. The united filtrates are evaporated to dryness, the residue dissolved in dilute hydrochloric acid, and hydrogen sulphide passed into the hot solution. The nickel is precipitated from the filtrate with sodium hydroxide, converted into nickel chloride, dissolved in water, and made up to a definite volume. In this solution, the nickel is estimated colorimetrically using α -dimethylglyoxime, which forms a scarlet-red compound with nickel in the presence of ammonia (compare Tschugaeff, *Abstr.*, 1905, ii, 613).

E. F. A.

Reaction of Iron Salts with Sodium Sulphide. LUCIEN L. DE KONINCK (*Chem. Centr.*, 1906, i, 964—965; from *Bull. Soc. chim. Belg.*, 19, 181—189).—The reaction with sodium sulphide is quite as delicate a test for iron as the ferrocyanide reaction, and it does not matter whether the iron is in the ferrous or ferric state. In extremely dilute solutions, a brown coloration changing to green is observed. The best condition for the appearance of the green colour is a proportion of 800—320 mols. of alkali sulphide to 1 atom of iron. In the presence of sodium chloride or sulphate, the formation of the green compound is retarded, and it then disappears sooner than usual. In the presence of zinc, the precipitate is coloured brown owing to the

presence of the brown modification of the ferrous sulphide, but in the case of aluminium or magnesium, the green variety is carried down. Cadmium causes a yellowish-green coloration which soon fades.

L. DE K.

Separation of Iron from Manganese, Nickel, Cobalt, and Zinc by the Acetate Process. W. FUNK (*Zeit. anal. Chem.*, 1906, 45, 181—195).—The solution, which should contain about 0.2 gram of ferric iron, is evaporated on the water-bath with addition of about 0.7 gram of potassium chloride until the mass is nearly dry; care must, however, be taken not to expel the free hydrochloric acid completely. The residue is now dissolved in 20 c.c. of water and then mixed with a solution of sodium acetate containing about twice the theoretical quantity required. After diluting to about 500 c.c., the whole is heated to 60—70°, when the iron is precipitated completely as basic acetate, which is then washed with hot water. The other metals are determined in the filtrate.

L. DE K.

Vanadium as a Steel-making Element. J. KENT SMITH (*J. Soc. Chem. Ind.*, 1906, 25, 291—295).—A summary of the static and dynamic properties of various types of vanadium steel. The following method is recommended for the rapid estimation of vanadium in steel. One gram of the sample is dissolved in about 40 c.c. of 25 per cent. nitric acid; when cool, the solution is agitated momentarily with 2 grams of sodium bismuthate and filtered quickly; the filtrate and washings are decolorised with a few c.c. of strong ferrous sulphate solution and 10 c.c. of freshly-prepared hydrogen peroxide solution, and the whole is then made up to 100 c.c. The amount of vanadium present is then estimated by comparing the colour of the solution with comparison tubes.

P. H.

Experiments with New Apparatus for Elementary Analysis (Dennstedt and Heraeus Furnaces). DAVID HOLDE (*Ber.*, 1906, 39, 1615—1622).—A critical discussion from various points of view of the Dennstedt and Heraeus (electric) furnaces. With the former, good results have not been obtained so far when cinnamic acid, anthraquinone, or benzene was used.

J. J. S.

Simplified Elementary Analysis. MAX DENNSTEDT (*Ber.*, 1906, 39, 1623—1627. Compare Abstr., 1903, ii, 103; 1905, ii, 202, 651).—In reply to Holde (preceding abstract), several practical details are given for obtaining good results with the Dennstedt furnace.

J. J. S.

Ultimate Analysis of Organic Substances. HUGO HERMANN (*Zeit. anal. Chem.*, 1906, 45, 236—238. Compare Abstr., 1905, ii, 767).—A final reply to the criticisms of Dennstedt (this vol., ii, 200).

L. DE K.

Electrical Method for the Simultaneous Estimation of Hydrogen, Carbon, and Sulphur in Organic Compounds. HARMON N. MORSE and C. W. GRAY (*Amer. Chem. J.*, 1906, 35, 451—458).—A claim for priority is made with reference to the electrical method for the combustion of organic compounds devised by Morse and Taylor (*Abstr.*, 1905, ii, 480) in view of the similar method recently described by Carrasco (*this vol.*, ii, 200).

A method is now described for the simultaneous estimation of carbon, hydrogen, and sulphur. The apparatus employed is a modification of that of Morse and Taylor (*loc. cit.*). The sulphur dioxide is absorbed by means of a weighed quantity of pure lead peroxide contained in a platinum boat, which is open at one end in order to facilitate contact between the products of combustion and the peroxide. The rolls of copper gauze which, in the original apparatus, preceded and followed the boat containing the substance to be analysed are replaced by asbestos plugs. In front of the combustion tube, for the purpose of completing the absorption of nitrogen oxide, is placed a glass tube, which is filled with asbestos, covered with lead peroxide, and is surrounded by an electrically-heated graphited porcelain tube about 300 mm. long, provided with an asbestos covering. The glass tube is connected on one side to the combustion tube, and on the other to the usual absorption apparatus for water and carbon dioxide.

The quantity of lead oxide (PbO) yielded by unit weight of the peroxide is estimated before commencing the experiment. After a combustion has been made, the amount of sulphur absorbed is estimated by reducing the peroxide in the boat to the oxide (PbO) by heating it in a current of air or nitrogen until the weight remains constant. The excess in weight is due to sulphur trioxide, which is present as lead sulphate.

The results of the combustion of some organic compounds containing sulphur are given, which show that the method is satisfactory. The apparatus and method of working are fully described with the aid of a diagram. E. G.

Use of Cobaltic Oxide in the Combustion of Coals. FRANZ NEUMANN (*Chem. Centr.*, 1906, i, 1186; from *Woch. ges. Brauw.*, 23, 98).—An attempt to burn coal rapidly in the improved Dennstedt apparatus (*Abstr.*, 1905, ii, 651) by mixing the sample with twice its weight of cobaltic oxide. Although the hydrogen estimation is satisfactory, the results for carbon are too low. L. DE K.

Estimation of Methyl Alcohol in Solutions of Formaldehyde by means of Chromic Acid. OSKAR BLANK and HERMANN FINKENBEINER (*Ber.*, 1906, 39, 1326—1327).—The authors describe a method of estimating methyl alcohol in commercial formaldehyde, which generally contains from 12 to 18 per cent. of methyl alcohol. A weighed amount of the solution of formaldehyde is added to a solution of standard chromic acid to which sulphuric acid has been added. After twelve hours at the ordinary temperature, the solution is diluted; to an aliquot portion, potassium iodide is added and the solution then titrated with standard sodium thiosulphate solution.

A. McK.

Detection of Mineral Acids in Wines. CH. BILLON (*Ann. Chim. anal.*, 1906, 11, 127—131).—The total alkalinity of the ash is determined by adding an excess of standard sulphuric acid, boiling to expel carbon dioxide, and titrating the free acid with standard alkali. A same amount of the sample is then treated in the usual manner with a mixture of equal portions of alcohol and ether, or, better still, two parts of alcohol and five parts of ethyl acetate. The precipitate thus obtained is collected and ignited, and the alkalinity of the ash is then determined.

If the first alkalinity is greater than or equal to the second, mineral acid is absent, but if smaller the sample contains an amount of mineral acid equal to the difference in alkalinity.

In the case of very acid and plastered wines, it is advisable to add to the sample 5 grams of potassium chloride per litre. L. DE K.

Influence of the Lead Precipitate on the Polarisation of Sugar. WM. D. HORNE (*Chem. Centr.*, 1906, i, 969; from *Bull. Assoc. Chim. Sucr. Dist.*, 23, 635—637).—A reply to H. and L. Pellet (*ibid.*, 1905, ii, 1555). The amount of sugar carried down by the addition of basic lead acetate may be neglected. The use of the dry basic acetate of the constant composition $3\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2, 2\text{PbO}$, now obtainable, is recommended. With care, the filtrate is free from excess of lead. L. DE K.

Influence of the Lead Precipitate on the Polarisation of Sugar. HENRI PELLET and L. PELLET (*Chem. Centr.*, 1906, i, 969; from *Bull. Assoc. Chim. Sucr. Dist.*, 23, 638—639).—A reply to Horne (preceding abstract). The lead precipitate contains a varying proportion of sugar, more than is generally supposed. The use of the dry basic acetate will probably be advantageous. Further experiments with raw cane-sugars will be communicated. L. DE K.

Two New Methods for the Estimation of Dextrose. CARL ARNOLD (*Ber.*, 1906, 39, 1227—1228. Compare Glassmann, this vol., ii, 203).—Creatinine reduces potassium mercuri-iodide solution at the ordinary temperature, or alkaline mercuric cyanide solution when boiled. Glassmann's methods for the estimation of dextrose in urine must give erroneous results unless the creatinine is oxidised by cold potassium mercuri-iodide solution before the dextrose is estimated in the boiling solution. G. Y.

The Pavy-Sahli Sugar Titration [in Urine]. B. WAGNER (*Chem. Centr.*, 1906, i, 1189; from *Zeit. ärztl. Fortbild.*, 3, 79—83).—The urine is, if necessary, diluted to 25—50 times its volume and titrated with the following solutions: (a) 8.316 grams of crystallised copper sulphate in one litre; (b) 40.8 grams of potassium hydroxide, 40.8 grams of Rochelle salt, and 600 c.c. of ammonia made up to one litre. Before use, 5 c.c. of each solution are mixed and diluted with 30 c.c. of water; this represents 0.005 gram of dextrose.

The results obtained are quite as accurate as those obtained in the fermentation saccharometer. L. DE K.

Estimation of Glycogen. ALBERT DESMOULIÈRE (*J. Pharm. Chim.*, 1906, [vi], 23, 244—249, 281—285, and 332—336).—Ten grams of the finely-divided liver or other organ are placed in a 200 c.c. flask, 60 c.c. of water, 0.03 gram of sulphuric acid, and about 0.15 gram of pepsin are added, and the mixture kept at a temperature of 48° for six hours. 4.7 grams of sulphuric acid and 35—40 c.c. of water are now added, and the solution heated in a closed vessel to a temperature of 115—120° for an hour and a half. The solution is then cooled, a slight excess of mercuric nitrate is added, the mixture rendered slightly alkaline by the addition of sodium hydroxide solution, and the volume made up to 200 c.c. with water. After filtration, 100 c.c. of the filtrate are shaken with 5 grams of zinc dust and again filtered. Fifty c.c. of the filtrate are treated with sufficient sodium hydroxide to redissolve the precipitate of zinc hydroxide and the dextrose in the solution estimated by Fehling's method. One part of anhydrous dextrose is equivalent to 0.978 part of glycogen. A correction must be made for the volume of the mercury precipitate, and also for the quantity of dextrose occurring naturally in the liver. In the first case, the precipitate is collected on the filter, dried, and its volume measured, whilst the dextrose is estimated by boiling 40 grams of the finely-divided liver with several successive quantities of water, filtering the extracts into a litre flask, clarifying the solution with mercuric nitrate and sodium hydroxide, and diluting with water to the mark. The mixture is filtered, a portion of the filtrate is treated with zinc dust, and the dextrose estimated by Fehling's method. As the volume of the solution is large and the quantity of dextrose small, the influence of the volume of the mercury precipitate may in this case be neglected.

W. P. S.

Estimation of Acetone. ADOLF JOLLES (*Ber.*, 1906, 39, 1306—1307).—For the estimation of acetone, a standard solution of sodium hydrogen sulphite, containing from three to four times the requisite amount, is added to the solution of acetone. After thirty hours, the solution is titrated with standard iodine solution. The action $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3 + \text{NaHSO}_3 = \text{CH}_3\cdot\text{C}(\text{OH})(\text{SO}_3\text{Na})\cdot\text{CH}_3$ proceeds quantitatively.

A. McK.

Method of Distinguishing Fermentation Vinegar from "Vinegar Essence." EUGEN SCHMIDT (*Zeit. Nahr. Genussm.*, 1906, 11, 386—391).—Fermentation vinegar contains substances produced by the bacteria present (*Bacterium aceti* and *B. Kützingerianum*) which have chemical properties resembling those of the alkaloids. On this account, fermentation vinegar gives a turbidity when tested with a solution of iodine in potassium iodide, whilst "vinegar essence" (prepared from pure acetic acid) does not become turbid. If the amount of fermentation vinegar in a mixture is small, the latter may not yield a turbidity, but the residue obtained on evaporation will do so.

W. P. S.

Volumetric Estimation of Uric Acid by means of Iodine Solution. A. RONCHÈSE (*J. Pharm. Chim.*, 1906, [vi], 23, 336—340).—Uric acid may be estimated in urine as follows: 100 c.c.

of the urine are treated with 15 c.c. of ammonia and 15 grams of ammonium chloride. After the lapse of thirty minutes, the precipitate is collected on a filter and washed with a solution containing 150 c.c. of ammonia and 150 grams of ammonium chloride per litre. The precipitate is then washed off the filter with about 300 c.c. of water and dissolved by the addition of dilute acetic acid. Excess of potassium hydrogen carbonate or borax is added to the solution, and the latter titrated with standardised iodine solution. One c.c. of $N/10$ iodine solution is equivalent to 0.084 gram of uric acid. To the quantity of uric acid found per litre of urine is added 0.01 gram to correct for the solubility of the acid in the volume of ammonium chloride solution used.

W. P. S.

Fat Analysis. WILHELM FAHRION (*Chem. Zeit.*, 1906, 30, 267—268. Compare Abstr., 1904, ii, 217, 788).—A series of suggested improvements in some well-known methods relating to fats.

1. *Estimation of Fat in Milk*.—Instead of shaking out a mixture of 10 c.c. of milk, 10 c.c. of alcohol, and 1 c.c. of ammonia with 25 c.c. of ether and 25 c.c. of light petroleum and then evaporating an aliquot part of the ethereal layer, it is proposed that the milk should be shaken with three successive portions of 25, 15, and 15 c.c. of the ether-petroleum mixture and the whole of this then evaporated to dryness.

2. *Estimation of Water and Fat in Butter*.—The water is estimated by heating the butter over a small Bunsen flame with constant stirring; the loss represents the water. The mass is then extracted with light petroleum, the residue collected partly on a weighed filter and partly left in the basin, well washed, dried at 105° , and weighed. The fat is found from the loss, but may, of course, also be obtained by direct weighing. The insoluble matter may then be burnt to ash.

3. *Estimation of the Total Fatty Acids in Butter Fat, Cocoa Fat, and Palm Kernel Oil*.—Butter is saponified as usual with alcoholic potassium hydroxide, and the liberated fatty acids are dissolved by shaking with light petroleum or repeatedly with ether. The solvent is allowed to evaporate spontaneously, the residue is dissolved in alcohol and carefully neutralised with N /sodium hydroxide. The resulting soap solution is evaporated to dryness and the residue dried at 110° and weighed. If a represents the number of mg. of the soap and n the number of c.c. of alkali added, then $a - 22n$ represents the fatty acids.

4. *Estimation of the Inner Iodine Number*.—The crude ethereal solution of the liquid acids obtained in due course from the lead salts soluble in ether also contains any unsaponifiable matter. It is therefore recommended to shake it with a solution containing 2 grams of sodium hydroxide and a little alcohol. The alkaline layer is removed, acidified with hydrochloric acid, and shaken with light petroleum, which redissolves the oleic acid. On evaporation, this will leave an almost colourless oily residue.

L. DE K.

Detection of Coconut Oil in Butter. H. P. WIJSMANN and J. J. REIJST (*Zeit. Nahr. Genussm.*, 1906, 11 267—271).—The method

proposed is based on the comparative insolubility of silver octoate, the latter salt being precipitated from the ordinary Reichert-Meissl distillate and the quantity of silver required for the precipitation ascertained. The details of the process are: 5 grams of the sample are saponified with sodium hydroxide and glycerol, distilled, and the distillate titrated as in the Reichert-Meissl process. Forty c.c. of $N/10$ silver nitrate solution are added to the neutralised filtrate, the precipitate is collected on a filter, and washed until the filtrate amounts to about 200 c.c. Fifty c.c. of $N/10$ sodium chloride solution are then added to the latter and the excess of chloride titrated back with the silver solution, using potassium chromate as indicator. The number of c.c. of silver solution used, when increased by one-tenth, is termed the "first silver number."

Another 5 grams of the sample are similarly saponified and distilled. When 100 c.c. of distillate have been collected, 100 c.c. of water are added to the distillation flask and the distillation continued. This addition of water is once more repeated. The distillate, amounting to 300 c.c., is mixed, filtered, and 250 c.c. of the filtrate are neutralised. Forty c.c. of $N/10$ silver nitrate solution are added to the neutral solution, the precipitate is collected on a filter, and washed until the filtrate measures about 350 c.c.; 50 c.c. of $N/10$ sodium chloride solution are added and titrated back as described above. The number of c.c. of silver solution now used, increased by one-fifth, constitutes the "second silver number." In the case of pure butter, this will be equal to the first silver value, or even less owing to the slight solubility of the silver octoate in the larger volume of distillate. Should coconut oil be present in the sample, the second silver number will be larger than the first. From the results recorded it is seen that a butter with a Reichert-Meissl number of 28.4 gave a first silver number of 5.9 and a second silver number of 5.95. The addition of 5 per cent. of coconut oil to this sample raised these values to 6.4 and 7.3 respectively.

W. P. S.

Detection of Coconut Oil in Butter by the Silver Numbers. FERDINAND JEAN (*Ann. Chim. anal.*, 1906, 11, 121—124).—A criticism of the process introduced by Wijsman and Reijst (preceding abstract) which is based on the fact that in the case of butters adulterated with coconut fat the latter portion of the Reichert-distillate contains an excess of acids precipitable by silver nitrate.

The author concludes that although the process is a valuable one, a negative result does not always prove the purity of the samples.

L. DE K.

Cocoanut Oil. J. J. REIJST (*Chem. Centr.*, 1906, i, 1061—1063; from *Pharm. Weekblad.*, 43, 117—128, 151—163).—Of unsaturated acids, only oleic acid is present. The highest saturated acid, according to the author, is myristic acid; butyric acid is absent.

L. DE K.

Kreis' Reactions for the Detection of Stale Oils. HANS KREIS (*Ann. Chim. anal.*, 1906, 11, 143).—Polemical. A reply to Marcille's criticism (*ibid.*, 51).

L. DE K.

Rapid Estimation of Fat in Cocoas. TSCHAPLOWITZ (*Zeit. anal. Chem.*, 1906, 45, 231—235).—About 3 grams of the sample are put into a cylindrical flask holding 80 c.c., the neck of which is graduated to 0.2 c.c. and runs from 73 to 77 c.c. Ten to fifteen c.c. of alcohol are added and the mixture is heated to boiling. When cooled somewhat, an equal bulk of ether is added and the mixture again heated to boiling. When cold, the liquid is made up with ether to 77 c.c., and, after thorough mixing, allowed to settle. The volume of the liquid is now read off and 1 c.c. is deducted for the volume occupied by the cocoa. Fifty c.c. are now pipetted off and evaporated to dryness. The residual fat must be purified by redissolving in ether and filtering through a tube closed with a plug of cotton wool. Finally, the solution is evaporated to dryness in a weighed flask. L. DE K.

Adulteration of Linseed Cakes. H. ROGER (*Ann. Chim. anal.*, 1906, 11, 136—142).—The sample is deprived of oil and matters soluble in acid and alkali, and the crude cellulose thus obtained is examined microscopically for husks of ground-nuts or cocoa, poppy-cake, &c. For quantitative details, the original paper should be consulted. L. DE K.

Dutch Cheese. CECIL H. CRIBB (*Analyst*, 1906, 31, 105—109).—Of eighteen samples of Dutch cheese recently examined by the author, nine contained extremely small quantities of fat, the percentage amounts found varying from 1.64 to 5.36. The poor quality of these cheeses is due to the use of separated milk in their manufacture. The author considers that the above-mentioned cheeses should be returned as adulterated, although a prosecution instituted against the vendor of one sample failed, the magistrate ruling that the buyer had been supplied with cheese of the quality demanded, namely, Dutch cheese. W. P. S.

Collaborative Work on Tannin Analysis. FRITZ H. SMALL (*J. Soc. Chem. Ind.*, 1906, 25, 296—298).—Of all the methods proposed for the estimation of tannin, none are founded on accurate chemical knowledge; they are essentially empirical, and most of them fail to give concordant results. The American Leather Chemists' Association has examined many of the methods, and as the result of their investigation the hide-powder process is stated to be the most trustworthy, provided that certain conditions are adhered to. The hide-powder employed is treated with chrome-alum, washed, squeezed, and added in a moist state to the tannin solution under examination. The chrome-alum treatment not only converts the soluble portion of the hide into insoluble compounds without diminishing the power of the hide-powder to absorb vegetable tannins, but it equalises the absorptive power of two powders which, before treatment, were very unlike. A correction is made for the amount of water introduced by the moist hide-powder. The evaporation of the solutions and the drying of the residues are also sources of discordant results. The drying is probably done best under reduced pressure in order to prevent the decomposition of some of the substances present in the residues,

A combined evaporator and drier is described which gives good results. It consists of a copper steam-bath with a solid top, on which the dish rests, and a steam-jacketed cover provided with openings for ventilation, which fits down closely on to the copper top of the bath.

W. P. S.

Extraction of Tanning Materials for Analysis. FLETCHER P. VEITCH and H. H. HURT (*J. Amer. Chem. Soc.*, 1906, 28, 505—512).—Further experiments with the continuous extractor (Veitch, *ibid.*, 27, 724). The results in tannin are often several per cent. higher than those obtained by means of the extractors usually employed. The materials used in the investigation comprised various samples of sumach, oak bark, Quebracho wood, and hemlock bark; also chesnut wood, canaigre, chestnut oak bark, &c. For details, the tables in the original article should be consulted.

L. DE K.

Barium and Calcium Salts of Gallic, Protocatechuic, and Digallic Acids. HENRY R. PROCTER and H. G. BENNETT (*J. Soc. Chem. Ind.*, 1906, 25, 251—254).—An adverse criticism of Parker and Payne's process for the assay of tanning materials by means of titration with standard baryta (*ibid.*, 1904, 648).

L. DE K.

Examination of Writing Inks. LEWIS S. MUNSON (*J. Amer. Chem. Soc.*, 1906, 28, 512—516).—The chemical analysis should include the estimation of the sp. gr., total solids, ash, iron oxide, and sulphuric anhydride. When dealing with logwood ink, chromium should be estimated instead of iron. As a specimen of a good ink for permanent records may be given the following composition: 23.4 grams of tannic acid, 7.7 grams of gallic acid, 30 grams of ferrous sulphate, 10 grams of gum arabic, 25 c.c. of dilute hydrochloric acid (U.S.Ph.), 1 gram of carbolic acid, water up to 1 litre.

As practical tests are recommended the exposure to sunlight of stripes made with the sample, and the effects of reagents, sodium hypochlorite, alcohol, water on the stripes, these tests also to be applied to the sample previously diluted with its own bulk of water. In the case of copying inks, the copy should also be examined. For full details, the exhaustive table in the original should be consulted.

L. DE K.

Estimation of Cyanates in the Presence of Cyanides. WILHELM WILD (*Zeit. anorg. Chem.*, 1906, 49, 122—124).—The author shows, in agreement with Victor (Abstr., 1901, ii, 623), that cyanates can be accurately estimated in the presence of cyanides by precipitation of both salts from one portion of a neutral solution by means of silver nitrate, and by throwing down the chloride from another part of the solution acidified with nitric acid, in which silver cyanate is soluble; from the difference in the amounts of silver nitrate required, the amount of cyanate present can readily be calculated. Ewan (Abstr., 1904, ii, 371) has expressed the opinion that methods based on this principle are not trustworthy, owing to the

solubility of silver cyanate in water, but the author shows that this solubility is so much diminished by employing a considerable excess of silver nitrate that the error arising from this cause is negligible.

G. S.

*iso*Nitroso-reaction of Antipyrine (Phenyldimethylpyrazolone) and its most Important Derivatives. FRIEDRICH SPERLING (*Chem. Centr.*, 1906, i, 1118; from *Zeit. Oesterr. Apoth.-V.*, 44, 51—52).—The red coloration produced by the action of an excess of hot nitric acid on antipyrine, quoted by the German pharmacopœia, is due to the formation of nitro-antipyrine, but is not always distinctly apparent, and under certain conditions a brown coloration is formed; the latter is caused by secondary reactions which result in the formation of a new nitroso-compound.

Antipyrine and all its derivatives with the exception of aminoantipyrine give the following reaction. Two drops of fuming nitric acid are added to 2—3 c.c. of a 1 per cent. aqueous solution of antipyrine and then 5 c.c. of concentrated sulphuric acid cautiously added. A cherry-red ring is formed at the surface of contact, and when the layers are mixed the colour permeates the whole liquid. When phenol or resorcinol is present, a vigorous action takes place on adding the concentrated sulphuric acid. Concentrated nitric acid gives a violet coloration with dimethylaminoantipyrine, which becomes yellow on the addition of concentrated sulphuric acid; if the liquid is then cooled and nitric acid again added, the yellow coloration becomes more intense, and when concentrated sulphuric acid is poured into the mixture so as to form a separate layer, a brown ring is produced at the zone of contact.

E. W. W.

New Reagents for Alkaloids and their Microscopical Application. M. HERDER (*Arch. Pharm.*, 1906, 244, 120—132).—The precipitates which barium and cæsium mercuri-iodides produce with alkaloids are less soluble than those produced by potassium mercuri-iodide. If the reaction is carried out, not in water, but in aqueous 30 per cent. chloral hydrate, the precipitates are crystalline from the start, or soon become so; in this medium, oxalic acid is the only organic acid, of those which occur commonly in plants, which produces a precipitate with barium mercuri-iodide when the concentration of the acid is no greater than is usual in the juices of plants.

The formation of these crystalline precipitates can be observed under the microscope, and used thus to demonstrate and localise an alkaloid in an organ of a plant. Sections are cut not so thin but that one layer of cells in them remains uninjured. Several of these are laid in a drop of a solution of the reagent (both barium and cæsium mercuri-iodides were used) on an object glass, and covered with a cover glass, which is sealed round the edge with canada balsam to prevent evaporation. A similar slide, to serve as a blank, is prepared with sections which have first been extracted with 5 per cent. alcoholic tartaric acid. The slides are examined at intervals under the microscope, the examination being extended over twenty-four hours at least, if no precipitate forms before. The formation of a precipitate in the

slide proper conjoined with the absence of a precipitate in the blank slide is held to demonstrate the presence of an alkaloid.

Results are given of the examination by this method of different organs of *Fibraurea chloroleuca*, *Hydrastis canadensis*, *Strychnos nuxvomica*, *Cinchona ledgeriana*, and *Conium maculatum*. C. F. B.

Estimation of Caffeine by means of the Immersion Refractometer. JOSEF HANUS and KARL CHOCENSKÝ (*Zeit. Nahr. Genussm.*, 1906, 11, 313—320).—The strength of aqueous solutions may be estimated by means of the immersion refractometer (Abstr., 1903, ii, 610), as the refraction of such solutions is directly proportional to the quantity of caffeine present. The amount of caffeine in 100 c.c. of solution may be calculated from the equation: $x = (y - 15)/5$, where y is the scale reading observed and x the percentage of caffeine. Distilled water gives a scale reading of 15 at 17.5°, and all observations should be taken at this temperature if the above calculation is employed. It is also advisable to keep the room temperature as near 17.5° as possible. A table is given showing the scale readings of solutions containing from 0.02 to 1.0 per cent. of caffeine.

W. P. S.

Apparatus for the Complete Extraction of Liquids containing "Saccharin." MAURICE DUYK (*Ann. Chim. anal.*, 1906, 11, 82—84).—The apparatus consists of a glass cylinder on a foot. At the bottom is sealed a small swan-neck tube which serves to carry off the accumulating aqueous liquid. After covering the bottom with some water, a quantity of ether is introduced reaching to the neck of the side-tube. The solution to be extracted is put into a bulb, and by means of a capillary tube at the bottom the liquid runs in a very fine stream into the ether, and so parts readily with the "saccharin" contained in it. The aqueous liquid which runs through the side-tube is collected and again poured back into the bulb. The extraction is usually complete after three fillings.

L. DE K.

Estimation of Casein. HENRY V. ARNY and T. M. PRATT (*Amer. J. Pharm.*, 1906, 78, 121—128).—The following volumetric method is proposed: 20 c.c. of $N/10$ ferric-alum solution (48.1 grams per litre) are added to 25 c.c. of the milk at the ordinary temperature. Some water is added, the mixture shaken, then filtered, and the precipitate washed until the washings are free from iron. The filtrate is now acidified with hydrochloric acid, potassium iodide is added, and the liberated iodine titrated with $N/10$ sodium thiosulphate solution. The quantity of ferric-alum solution required to precipitate the casein present in the milk is thus ascertained. Results of experiments are given to show that the quantity of ferric-alum used is in direct proportion to the casein present, and that the other constituents of milk have no influence on the estimation. The ferric-alum solution must be standardised on samples of milk, the casein in which has been estimated by other methods.

W. P. S.

Optical Determination of Gliadin in Flours. MARION (*Ann. Chim. anal.*, 1906, 11, 134—135).—Ten grams of flour are treated with 50 c.c. of alcohol (73° French) and heated in a closed tube placed in a water-bath at 40—45° for fifteen minutes with frequent shaking. After cooling rapidly to 15—20°, the contents are emptied into a beaker and stirred for one to two minutes, with addition of 0.8 gram of animal charcoal. The liquid is filtered and examined in the 2-decimetre tube of the polariscope. The reading a (in minutes) should be made most carefully. $a \times 0.0722$ equals the percentage of gliadin. L. DE K.

Detection [of Horse and Foetal Flesh by the Glycogen Estimation. MAX MARTIN (*Zeit. Nahr. Genussm.*, 1906, 11, 249—266).—As the glycogen present in horse flesh remains unchanged for a long time, and that in foetal flesh disappears extremely slowly, whilst all the glycogen contained in beef, veal, and pork is decomposed in a few days after the animal has been slaughtered, it is possible by means of a determination of the glycogen to detect the presence of horse or foetal flesh in sausages, potted meats, &c. For this purpose, Pflüger's method (*Abstr.*, 1903, ii, 248) gives the most satisfactory results, and permits the detection of as little as 10 per cent. of horse flesh. Other sources of glycogen, such as starch, spices, &c., must, however, be taken into account. In smoked horse flesh, the glycogen is destroyed and the estimation is of no use. The unusual stability of glycogen in horse flesh may be related to the feeble fermentative properties of horse blood as compared with ox blood. W. P. S.

Composition of Preserved Eggs and Egg Substitutes. ADOLF BEYTHIEN and L. WATERS (*Zeit. Nahr. Genussm.*, 1906, 11, 272—274).—Genuine dried yolk of eggs yields about 55 per cent. of ether extract, 2.6 per cent. of total phosphoric acid, and 1.6 per cent. of lecithin-phosphoric acid, and its composition agrees generally with the published analyses of this article of food. Many substitutes, however, are on the market, and the analyses of the same are recorded in this paper. One such article gave only 11.23 per cent. of ether extract, and 0.327 per cent. of lecithin-phosphoric acid, and apparently consisted of a mixture of casein with about 33 per cent. of dried egg. Two other samples examined consisted of maize meal with 3 to 4 per cent. of yolk of egg and a little sodium hydrogen carbonate, artificial colouring matter also being present. W. P. S.

Method of Estimating Impurities in Cocoas and Chocolates. FRÉD. BORDAS and TOUPLAIN (*Compt. rend.*, 1906, 142, 639—641).—Solid impurities in cocoas or chocolates can be readily estimated by mixing the powdered residue obtained after removing the fat and the substances soluble in water with mixtures of carbon tetrachloride and benzene of varying densities, subjecting the mixture to centrifugal action, decanting, washing, and drying the floating impurity, and repeating the treatment on the precipitate, using a liquid of greater density. M. A. W.

General and Physical Chemistry.

Pyroluminescence of Quartz. VICTOR M. GOLDSCHMIDT (*Chem. Centr.*, 1906, i, 1372; from *Christiania Vidensk.-Selsk. Forhandl.*, 1906, No. 5, 1—9).—The pyroluminescence of quartz is not dependent on colour, odour, or the nature of the surrounding medium. It begins to be apparent at 150° and is most distinct about 250°. It is not affected by reducing the quartz to powder, but is destroyed by heating at about 400°. The luminescence is apparently phosphorescence which is accelerated by heat, since, although it cannot be excited by sunlight, electric sparks, or Röntgen rays, it is produced or regenerated by the radiation of radium compounds. The colour is not affected by the radiation in the latter case, but when quartz from Fevor was exposed to the action of cathode rays, it became at first slightly brown and fluorescent, then phosphoresced for a short time, and finally showed pyroluminescence for a long time at 320°. The phenomena are possibly caused by the presence of inorganic impurities such as sulphide of copper or other heavy metals, as Königsberger has suggested.

E. W. W.

Relation between Temperature and Depth of Colour of Certain Inorganic Substances. PAUL ROHLAND (*Chem. Zeit.*, 1906, 30, 375—378).—Although a number of substances exhibit an increase or diminution in the depth of their colour with rise or fall of temperature, it is not possible to detect any difference in composition by analysis.

P. H.

Spectrum Analysis. CARL FREDENHAGEN (*Ann. Physik*, 1906, [iv], 20, 133—173).—The metallic spectra obtained in the carbon monoxide flame are the same as those in the ordinary bunsen flame. The spectra are, however, quite different when a hydrogen-chlorine flame is used; the alkali metals and thallium yield no visible spectrum, whilst the metals of the alkaline earths, copper, and other heavy metals exhibit characteristic spectra.

The author's results make it probable that the chief series of potassium and sodium lines and the green line of thallium are oxide spectra, whilst the secondary series of potassium and sodium lines and the spark lines of thallium are due really to the metals themselves.

J. C. P.

Spectrum of Lanthanum. ERNST WOLFF (*Chem. Centr.*, 1906, i, 324—325; from *Zeit. wiss. Photograph. Photophys. Photochem.*, 3, 395—402).—The spectra obtained when two separate preparations of oxide and oxalate of lanthanum were introduced into a carbon arc have been found to be identical. Photographs were taken by means of a concave Rowland grating of 6.6 m. curvature and 16,000 lines per inch. The lines between 2477 and 5762 are given in a table in the original

paper and their relative intensities indicated. The band spectrum of lanthanum is also described.

E. W. W.

Arc Spectra of Neodymium and Praseodymium. MAX BERTRAM (*Chem. Centr.*, 1906, i, 1321; from *Zeit. wiss. Photograph. Photophys. Photochem.*, 4, 16—43).—The spectra obtained by introducing preparations of neodymium and praseodymium into an arc produced between carbon electrodes by a current of 6—8 amperes at 220 volts have been photographed by means of a Rowland grating of 6.6 cm. curvature and 16,000 lines per inch. The spectrum of iron was photographed on the same plate. The wave-lengths from the extreme ultra-violet to the D line are given in tables in the original paper.

E. W. W.

Absorption Spectra of Neodymium and Praseodymium Chloride. WILHELM RECH (*Chem. Centr.*, 1906, i, 734—735; from *Zeit. wiss. Photograph. Photophys. Photochem.*, 3, 411—428).—Solutions of the pure oxides of neodymium and praseodymium in hydrochloric acid were diluted until the absorption spectra no longer showed any bands; the solution of neodymium chloride thus obtained was 1/256 normal, and that of praseodymium chloride 1/512 normal. The solutions were contained in a glass tube, 20 cm. long, which was closed by quartz plates when the refrangible portion of the spectrum was examined. Zirconium light was employed. The whole spectrum was photographed by means of two Rowland concave gratings of 1 m. curvature, containing 20,000 lines per inch. The results, which are arranged in tables in the original paper, are compared with previous measurements.

E. W. W.

Absorption of the Vapours of Benzene and Some of its Derivatives in the Ultra-violet. L. GREBE (*Chem. Centr.*, 1906, i, 341; from *Zeit. wiss. Photograph. Photophys. Photochem.*, 3, 376—394).—The ultra-violet rays produced by a spark discharge between aluminium points immersed in water were passed through the vapour contained in a tube at the ordinary temperature or at 30°. The vapours of benzene, toluene, ethylbenzene, *p*-, *m*-, and *o*-xylenes, chloro-, bromo-, and iodo-benzenes, and aniline were examined. The lines of the spectrum of benzene are regularly arranged, but only traces of such regularity are apparent in the other cases. The spectra of ethylbenzene, toluene, chlorobenzene, and bromobenzene show certain relationships. In the case of isomeric compounds, the distance from the ortho-position appears to increase the absorption, and to cause a displacement towards the red end. The absorption bands of the liquids are displaced towards the violet in the spectra of the vapours.

E. W. W.

Fluorescence of Glass, Mica, and Quartz caused by Radiotellurium. HEINRICH GREINACHER (*Chem. Centr.*, 1906, i, 1395; from *Physikal. Zeit.*, 7, 225—228).—Since radiotellurium is able to excite fluorescence, the α -rays of radium must have a fluorescent action. The fluorescence is difficult to see with the naked eye, but is

rendered evident by means of photographs. The fluorescence of glass lies nearer to the ultra-violet than that of mica. E. W. W.

Influence of Light on the Crystallisation of Supersaturated Solutions. MAX TRAUTZ and ARNOLD ANSCHÜTZ (*Zeit. physikal. Chem.*, 1906, 55, 442—448).—From the observations made, no definite general conclusion can be drawn. The effects noticed by the authors may have been due to the temperature changes caused by the light. J. C. P.

Influence of Incandescent Gas Light on Certain Pharmaceutical Preparations. NICOLAAS SCHOORL and L. M. VAN DEN BERG (*Chem. Centr.*, 1906, i, 696; from *Pharm. Weekblad*, 1906, 43, 47—49).—The authors have observed the effect of incandescent gas light on a number of substances contained in white or brown glass bottles when placed at a distance of 10 cm. from the burner and kept at a temperature of about 40° for 478 hours. Chloroform was not affected under these circumstances, whilst bromoform was decomposed only in the white glass bottles, with the formation of bromine and hydrogen bromide; solid iodoform behaved in the same way, but a 5 per cent. alcoholic solution was turned dark brown both in the white and in the brown glass bottles. A noticeable effect was also produced even when the substances were placed at 2 to 3 metres from the source of light. Chloral hydrate also after some time gave small quantities of hydrogen chloride. Resorcinol and pyrogallol were only discoloured where they came in contact with the glass, the action in this case being no doubt due to the combined action of the light and the alkali of the glass.

P. H.

Definition of Radioactivity. KARL SCHAUM (*Chem. Centr.*, 1906, i, 306—307; from *Zeit. wiss. Photograph. Photophys. Photochem.*, 3, 409—410).—The author compares his definition of radioactivity (*ibid.*, 2, 213) with that of Soddy (*Jahrb. Radioakt.* II, 1) and also points out that at the time these definitions were made it was not known that the α -rays are not ions.

E. W. W.

Radioactivity of Metals and their Salts. NORMAN R. CAMPBELL (*Proc. Camb. Phil. Soc.*, 1906, 13, 282—287).—The paper contains results of work undertaken with the object of finding whether the radioactivity of compounds is an additive function of that of the constituents. The compounds examined were lead, lead sulphate, lead oxide; tin, tin sulphide; bismuth, bismuth oxide; mercury, mercurous and mercuric oxides. The author considers that the measurements confirm the theory that the activity is an atomic property, but the experimental errors are comparatively so large that further work is necessary, both to establish this and to determine whether the activity varies with the valency (compare *Abstr.*, 1905, ii, 296). L. M. J.

Distribution of Radium in the Earth's Crust, and the Earth's Internal Heat. ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1906, A, 77, 472—485. Compare *Abstr.*, 1905, ii, 787).—With the object of determining the average distribution of radium in the earth's crust,

samples of numerous typical igneous rocks were examined and a few experiments were also made with meteorites. The results were fairly uniform and indicated from 1.8 to 25×10^{-12} grams per c.c. of rock, granites, as a rule, containing a higher proportion than basic rocks. A stony meteorite was found to contain about the same proportion of radium as terrestrial rocks of corresponding composition, but no appreciable quantity of the element is present in iron meteorites.

If it is assumed that the earth is in thermal equilibrium, and that the whole of the internal heat is due to radium, the mean proportion of this element cannot much exceed 1.75×10^{-13} grams per c.c., taking the observed temperature gradient near the surface as the basis of calculation. Since the average amount present in surface rocks is at least 5×10^{-12} grams per c.c., it follows that only 1/30 of the earth's volume can consist of material similar to that on the surface. If the central part is composed of material free from radium, this gives about 45 miles as the thickness of the earth's crust—a result which at first sight seems surprising, but is in substantial agreement with Milne's recent estimate of thirty miles (Bakerian Lecture, 1906), based on the velocity of propagation of earthquakes through the earth's interior.

From the data here given, and on the assumption that the moon is largely composed of rock, it is calculated that the temperature gradient at its surface is eight times greater than at the earth's. Since gravity is so much less in the former case, conditions on the moon should be particularly favourable for the display of volcanic activity. G. S.

Indirect Proof of the Presence of Radium in Carlsbad Hot Springs. JOSEF KNETT (*Chem. Centr.*, 1906, i, 400; from *Sitzungsber. Akad. Wiss. Wien.*, 113, 753—762).—Although no trace of barium is given in the analyses of the Carlsbad hot springs, the water from these sources is found in course of time to deposit radioactive crystals of barium sulphate. This “radiobaryte” probably contains radium sulphate, and is the only known radioactive mineral which is free from uranium or thorium. E. W. W.

Action of Radium and other Salts on Gelatin. W. A. DOUGLAS RUDGE (*Proc. Camb. Phil. Soc.*, 1906, 13, 258—259).—If a radium salt is sprinkled on some sterilised gelatin, it gives rise to a nebulous patch something like a fungus or mould, and appears of cellular structure when viewed under the microscope. Some of the “cells” appeared nucleated and some were dumb-bell shape, but no “cell” was actually found to divide. It was found that barium salts give phenomena which can scarcely be distinguished from those caused by radium, whilst similar results are obtainable with lead and strontium salts. If a solution of a barium or radium salt is added to liquefied gelatin, a precipitate is formed, and if the gelatin is then filtered under pressure through a porous tube, it no longer gives any of these phenomena with radium, but becomes again active if a small quantity of a soluble sulphate is added. There is, therefore, no specific action of the radium on gelatin, the apparent cell formation being merely due to formation of precipitates of insoluble sulphates. Other

mucilaginous substances yield similar results if they contain sulphates.

L. M. J.

Radioactivity of the Salts of Radium. BERTRAM B. BOLTWOOD (*Amer. J. Sci.*, 1906, [iv], 21, 409—414).—The author has determined the ratio of the activity of radium when it contains its total equilibrium quantity of emanation and disintegration products to the activity when these products have been removed. Three films of radium-barium bromide were used, and the ratios found were 5.59, 5.68, and 5.67. It was found by Bragg and Kleeman (*Abstr.*, 1905, ii, 5) that the ranges at atmospheric pressure of the α -particles from radium and its disintegration productions are respectively: radium, 3.5 cm.; emanation, 4.23 cm.; radium A, 4.83 cm.; radium C, 7.06 cm. The sum of these numbers is 19.6, that is, 5.6 times the range of the α -particle from radium itself, and from the coincidence of the numbers the author considers it highly probable that the α -ray activities of the different products are proportional to the ranges of their α -particles.

L. M. J.

Ionisation produced by α -Rays. HOWARD L. BRONSON (*Phil. Mag.*, 1906, [vi], 11, 806—812).—It appears that the α -particle loses its energy very rapidly near the end of its path by collision with the gas molecules, and that a thickness of air of 7.2 cm. is sufficient for complete absorption. The author's experiments further show that radium B does not give off α -particles, none, at any rate, of sufficient velocity to ionise air.

J. C. P.

Secondary Röntgen Radiation. CHARLES G. BARKLA (*Phil. Mag.*, 1906, [vi], 11, 812—828. Compare Bumstead, this vol., ii, 141).—In general, the secondary radiations from light substances are, in respect of absorption, very similar to the primary radiations from which they are produced, but the secondary radiations from heavy substances are more easily absorbed. The character of the secondary radiation in the latter cases does not depend to any appreciable extent on the intensity of the primary radiation. When the absorbability of the secondary radiation is plotted against the atomic weight of the element used as radiator, the curves obtained show a rise and fall, and are similar to those recorded by McClelland in his experiments on the secondary radiations from substances exposed to β - and γ -radiation rays.

J. C. P.

Secondary Radiation from Compounds. III. JOHN A. MCCLELLAND and F. E. HACKETT (*Sci. Trans. Roy. Dubl. Soc.*, 1906, [ii], 9, 27—36. Compare *Abstr.*, 1905, ii, 495, 496).—Observations on the oxides, sulphides, and halides of various metals indicate that the intensity of the secondary radiation from compounds submitted to the action of the β - (and γ -) rays of radium is an additive atomic property. The intensity for any compound can be calculated if the radiating powers of the constituent elements are known.

If the radiating power of hydrogen is deduced from the experimental data for compounds such as water, benzene, toluene, and aniline, a

very small positive value is obtained in some cases, in others a small negative value. The value for hydrogen is evidently very small, and this result agrees with the previous observations, according to which the radiating power diminishes as the atomic weight diminishes.

The examination of compounds of barium, cerium, and didymium shows that whilst the radiating power of these elements fits in with the general rule, there is very little difference between the separate values.

From the close relationship between the intensity of the secondary radiation and the atomic weight, the author supposes that the β -particles must actually come from the atoms, and cannot possibly be free electrons immediately previous to emission. H. M. D.

Spectrum of the Light of Canal Rays in Nitrogen and Hydrogen. JOHANNES STARK and W. HERMANN (*Chem. Centr.*, 1906, i, 812; from *Physikal. Zeit.*, 7, 92—97. Compare this vol., ii, 321).—The intensity of the nitrogen lines of the spectrum of the canal rays is not very great when compared with the first and second band spectrum, but in hydrogen the line spectrum is more brilliant than the band spectrum; the greater the velocity of the canal rays the more intense the lines. The effect of impurities, which readily form positive ions, such as hydrogen, mercury, or aluminium (from the cathode), is easily seen in the spectrum. E. W. W.

Moser Rays. N. PILTSCHIKOW (*Chem. Centr.*, 1906, i, 631—632; from *Physikal. Zeit.*, 1906, 7, 69—70).—The so-called Moser rays, which are emitted from metallic surfaces and are capable of passing through thin layers of paper, celluloid, gelatin, or aluminium, are divided by the author into three groups: firstly, the positive rays which decompose silver bromide; secondly, the negative rays which are able to restore silver bromide which has been exposed to light, and thirdly, the neutral rays which have no effect on this salt. Positive rays are emitted by manganese, aluminium, zinc, cadmium, tellurium, selenium, iron, cobalt, nickel, silicon, boron, lead, tin, zirconium, platinum, palladium, and colloidal silver, negative rays by osmium, tantalum, and ?titanium, whilst copper and brass emit neutral rays; the elements gold, iridium, rhodium, ruthenium, molybdenum, and mercury emit practically no Moser rays. The intensity of the radiation increases directly with the moisture of the atmosphere, whilst in a Geissler vacuum the radiation practically ceases. The radiation may be deflected by a stream of air, but is unaffected by electric or magnetic fields. Both positive and negative rays excite secondary radiation. Moser rays are not vapours, as the rays emitted from platinum are not absorbed by silver foil with the formation of an alloy. The rays are able to pass through the skin and may be of therapeutic value. P. H.

Some Properties of Actinium. ANDRÉ DEBIERNE (*Chem. Centr.*, 1906, i, 326; from *Physikal. Zeit.*, 7, 14—16. Compare Abstr., 1903, ii, 257, 348; 1904, ii, 223, 729; 1905, ii, 623).—In reference to Godlewski's description of the successive products of actinium (Abstr.,

1905, ii, 497), priority is claimed in regard to several facts. The author also protests against Marckwald's assertion (Abstr., 1905, ii, 497) that actinium is derived from emanium. Giesel's emanium is identical with actinium, and the name actinium must be reserved for the parent substance. E. W. W.

Radioactivity of Thorium Minerals and Salts. BERTRAM B. BOLTWOOD (*Amer. J. Sci.*, 1906, [iv], 21, 415—426).—Various authors have claimed to have found inactive thorium, but Strutt obtained thorium emanation from all the thorium-bearing minerals he examined (compare Abstr., 1905, ii, 95; *ibid.*, 787). Hahn obtained a highly active substance, radiothorium (Abstr., 1905, ii, 789), from thorium minerals, which he suggests is a disintegration product of ordinary thorium, and is the active principle; as it seems probable that in the natural minerals equilibrium between thorium and radiothorium would have been attained, the author has determined the α -ray activity due to thorium in various minerals, and then the activity per gram of thorium. The minerals employed were thorianite, thorite, orangite, and monazite. The activity was determined and the percentage of uranium and thorium; from the total activity, that due to the uranium present was subtracted and the activity per gram of thorium then calculated: the values so obtained agreed for the four minerals, that is, the specific radioactivity of thorium is constant. For thorium salts obtained from various sources, this constancy does not exist and the specific radioactivity is frequently less than one-half that of the natural compound. This, the author considers, supports the suggestion that the activity is due to the presence of radiothorium, which is largely removed in the commercial methods of preparing pure thorium salts. It is pointed out that although radiothorium oxalate is insoluble in excess of ammonium oxalate, yet when accompanied by thorium it is readily soluble, and that such peculiarities are common with the radioactive elements. The disintegration of the thorium to radiothorium is probably a rayless change. L. M. J.

Radioactivity of Thorium. H. M. DADOURIAN (*Amer. J. Sci.*, 1906, [iv], 21, 427—432).—Experiments were made to determine the ratio of the activity of thorium minerals and salts to the quantity of thorium present. The results are in entire accord with those of Boltwood (preceding abstract), the ratio being constant for the minerals, but lower and variable for the salts. As one of the salts prepared three years previously was notably deficient in radiothorium, the rate of recovery of radiothorium must be very slow, and the half value period cannot be less than two years. L. M. J.

Relation between Radioactivity and Composition of Thorium Compounds. HERBERT N. MCCOY and W. H. ROSS (*Amer. J. Sci.*, 1906, [iv], 21, 433—443. Compare preceding abstracts).—A constant ratio between activity and the amount of thorium was found for the thorium minerals examined and for the thorium dioxide obtained from them. Lower values were obtained, however, for thorium salts. Experiments made in order to obtain inactive thorium

were not successful. The authors consider it clearly proved that the activity of thorium compounds cannot be due to accidental impurities, but must be due to disintegration products of thorium itself.

L. M. J.

Absorption of Thorium Emanation. ALFRED KLAUS (*Chem. Centr.*, 1906, i, 177; from *Physikal. Zeitschr.*, 1905, 6, 820—825).—On account of the rapid decay of thorium emanation, it is difficult to measure its absorption. For petroleum and water, the absorption coefficients have been determined by measuring the conductivity of the air in a Rutherford vessel with and without the absorbing liquid. At 19°, the values are 5.0 and 1.05 respectively. The ratio of the coefficients is much greater in the case of radium emanation (20 : 1).

H. M. D.

Some Properties of the α -Rays from Radiothorium. I. OSKAR HAHN (*Phil. Mag.*, 1906, [vi], 11, 793—805. Compare Hahn, Abstr., 1905, ii, 432, 789; Ramsay, Abstr., 1905, ii, 789).—The experiments indicate that two α -ray products are present in the active deposit of radiothorium, and not one as was supposed previously. The new α -ray product thus indicated is named "thorium C," but it is not possible to determine which of the two sets of α -rays, of range 8.6 cm. and 4.7 cm. respectively, is due to the new product. The α -rays from the active deposit of thorium are deflected both by a magnetic and an electric field, and to about the same extent as the rays from radium C. The following table gives a list of the thorium products so far as they are known :

Product.	Nature of rays emitted.	Time for product to be half transformed.
Thorium	Probably rayless	About 10^9 years
Radiothorium	α -rays	?
Thorium X	α -rays	4 days
Emanation	α -rays	54 seconds
Thorium A	rayless	10.6 hours
Thorium B	α -rays	1 hour
Thorium C	α -, β -, γ -rays	a few seconds (?)

J. C. P.

α -Particles of Uranium and Thorium. WILLIAM H. BRAGG (*Phil. Mag.*, 1906, [vi], 11, 754—768).—The author discusses the magnitude of the ionisation current due to a layer of radioactive material scattered on the floor of an ionisation chamber, and covered by a uniform sheet of metal foil. The result is expressed in a formula. Experiments have been carried out showing (1) that the values of the current in

various cases, calculated from the formula, agree very well with the results of observation; (2) that the ranges of the α -particles of uranium and thorium are very nearly equal to the range of the α -particle of radium; (3) that the rate at which thorium atoms break down is nearly 0.19 of the similar rate for uranium. J. C. P.

Photoelectric Behaviour of Anthracene. ALFREDO POCHETTINO (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 355—363).—Three samples of anthracene, varying in colour and degree of purity, exhibited fluorescence of different colours when illuminated by the light of the voltaic arc. The purest one was white and gave a violet fluorescence. The photoelectric effect of anthracene diminishes as time goes on, possibly owing to conversion of the anthracene into dianthracene (Luther and Weigert, *Abstr.*, 1905, ii, 785), but it recovers its original value when the anthracene is stored in the dark. In the fused state, or when dissolved in benzene, anthracene exhibits the same photoelectric effect as it does in the solid form; solid phenanthrene has a greater photoelectric effect than its solution in benzene. A magnetic field affects the phenomenon in such a way that, if the lines of force are perpendicular to the direction of emission, the conductivity is diminished by about 10 per cent. T. H. P.

Electrochemical Calculations. JOSEPH W. RICHARDS (*Chem. Centr.*, 1906, i, 1393; from *J. Franklin Inst.*, 161, 131—142, 161—171).—The heat absorbed in chemical work per equivalent = $96.540 \times 0.2385 \times$ potential difference. The thermochemical constants of lithium, rubidium, potassium, &c., fluorine, chlorine, bromine, iodine, sulphur, selenium, and of the groups OH, SH, SeH, ClO, &c., calculated on the assumption that the hydrogen constant = 0, are given in tables in the original paper. E. W. W.

Action of Depolarisers. FRITZ WEIGERT (*Zeit. Elektrochem.*, 1906, 12, 377—382).—The depolarisation of a platinum cathode charged with hydrogen is considered. The pressure of the hydrogen, due to a given potential difference, is obtained from Nernst's formula. At potentials smaller than that required to liberate hydrogen gas, the current passing is due to the reaction between hydrogen and the oxidising agent in the solution. The velocity of this reaction is a function of the pressure of the hydrogen and of the concentration of the oxidising agent in the solution in immediate contact with the cathode. If depolarisation is so rapid that the depolariser at the cathode is used up, the current passing is fixed by the velocity with which the depolariser can diffuse to the cathode. The theoretical curve showing the connection between current and cathode potential is given. By employing a rotating cathode, the author has been able in a number of cases to obtain experimental curves very closely resembling the theoretical one. The depolarisers used were iodine, bromine, permanganate, iodate, bromate, oxygen, dichromate, persulphate, and hydrogen peroxide. T. E.

Cathodic Evaporation of Metals in Attenuated Gases. VOLKMAR KOHLSCHÜTTER and RUD. MÜLLER (*Zeit. Elektrochem.*, 1906, 12, 365—377).—The quantity of metal thrown off from a cathode in an atmosphere of a gas at a pressure of 0.2 to 1.5 mm. of mercury is shown to depend, not only on the nature of the metal, but also on that of the gas. Aluminium, iron, copper, platinum, gold, cadmium, and silver are studied in atmospheres of hydrogen, helium, argon, nitrogen, and oxygen. Aluminium evaporates in argon only, iron evaporates to a small, almost equal extent, in all the gases; the same is true of copper, although the evaporation is larger. Silver gives a large deposit in argon. Platinum gives relatively small deposits in helium, hydrogen, and argon, larger ones in nitrogen and oxygen. The evaporation of gold, in the gases, increases in the order, helium, hydrogen, nitrogen, oxygen, argon.

The pressure of the gas in the tube changes during the discharge. Three types of curve were found. With aluminium, cadmium, and iron in hydrogen, the increase of pressure is proportional to the time during which the discharge has passed. This is explained by electrolysis of a layer of hydroxide on the surface of the metal. With oxygen and nitrogen the pressure decreases for all the metals, probably owing to chemical combination of the gases and metals. In the third type, the pressure becomes constant after a short time, an equilibrium being reached it would seem.

The view is advanced that the evaporation is due to the formation of endothermic compounds of metal and gas at the high temperature reached by the gas molecules in the path of the discharge; at lower temperatures these compounds decompose, depositing the metals on the glass walls of the tube.

T. E.

Conductivity of Fused Salts. KURT ARNDT (*Zeit. Elektrochem.*, 1906, 12, 337—342).—The pure salts were fused in a porcelain U-tube, heated in an electrical resistance furnace, and the electrical conductivity measured by means of an alternating current and telephone. The porcelain was not attacked appreciably by the fused salts, with the exception of sodium carbonate and, to a much smaller extent, potassium carbonate. The conductivity in reciprocal ohms for a cube of 1 cm. is expressed by the formula $K = a[1 + b(t - 900^\circ) - c(t - 900^\circ)^2]$. The values of the constants are

	<i>a.</i>	<i>b</i> × 10 ⁴ .	<i>c</i> × 10 ⁶ .
Potassium chloride	2.38	8.4	0
Sodium chloride	3.66	8.7	0
Calcium chloride	2.32	15.1	0.9
Strontium chloride	1.98	16.7	1.0
Barium chloride	1.71	19.2	2.0
Sodium sulphate	2.23	12.2	0
Potassium carbonate	1.95	19.9	0
Potassium sulphate	1.44	14.0	0

The numbers for potassium sulphate are uncertain, as measurements were only made over a small interval of temperature. The conductivity of sodium carbonate was measured between 865° and 885°, and the

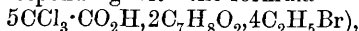
values given are 2.92 at 850° and 3.10 at 900° . The conductivities of sodium and potassium chlorides may be expressed very exactly by the formulæ $0.00312T$ and $0.00203T$ respectively (T being the absolute temperature). This is not the case with the salts containing bivalent ions. The melting points of the salts used were found to be: potassium chloride 775° , sodium chloride 805° , calcium chloride 774° , strontium chloride 873° , barium chloride 950° , sodium sulphate 883° , potassium carbonate 900° .

The melting point of sodium carbonate was taken as 852° , and this point was used in standardising the thermo-element used. T. E.

Conductivity of Ammonium Sulphate in Mixtures of Sulphuric Acid and Water. G. BOIZARD (*Compt. rend.*, 1906, 142, 1082—1084).—When ammonium sulphate is dissolved in mixtures of sulphuric acid and water, solutions are obtained which may have a greater or smaller conductivity than the solvent. The magnitude of the difference between the two conductivities is dependent both on the concentration of the sulphate and on the temperature. Tables of results illustrating this are given in the original. Similar effects are produced generally (1) by the solution of sulphates, acid sulphates, mineral or organic acids and their alkali salts in mixtures of sulphuric acid and water, and (2) by the solution of nitric or phosphoric acid in water. On the other hand, solutions of various salts in mixtures of acetic or formic acid with water are invariably better conductors than the mixtures alone. T. A. H.

Compounds of Dimethylpyrone with Trichloroacetic Acid. Electrical Conductivity of Solutions in Ethyl Bromide, Chloroform, and Benzene. WLADIMIR A. PLOTNIKOFF (*Ber.*, 1906, 39, 1794—1804. Compare Abstr., 1905, i, 77; ii, 433; this vol., ii, 144).—The conductivities of the normal and the acid salts are tabulated, and also plotted graphically; the former salt has the smaller conductivity. The conductivity of the salts at great dilutions is very small, since they decompose into trichloroacetic acid and dimethylpyrone, which are practically non-electrolytes in these solvents.

When the solution in ethyl bromide contains 54.4 per cent. of trichloroacetic acid, 16.2 per cent. of dimethylpyrone, and 29.4 per cent. of the solvent (corresponding with the formula



the whole liquid solidifies to a crystalline mass; a similar result occurs in benzene.

The constitutions of the salts are discussed, and are shown to be most in harmony with Werner's theory, assuming the co-ordination number of oxygen to be six.

Contrary to statements in the literature, hydrocarbons and their halogen-substituted derivatives are proved to have an ionising-capacity (compare also Abstr., 1902, ii, 639). C. S.

The Kinetic Theory of the Electron as the Basis of the Electron Theory of Radiation. THOMAS TOMMASINA (*Chem. Centr.*, 1906, i, 631; from *Physikal. Zeit.*, 1906, 7, 56—62).—The paper con-

tains a summary of the author's speculative views on the above subject.
P. H.

Velocities of the Ions of Alkali Salt Vapours at High Temperatures. HAROLD A. WILSON (*Phil. Mag.*, 1906, [vi], 11, 790—793. Compare Abstr., 1899, ii, 722; 1901, ii, 490).—A short *résumé* of previous work, and a criticism of Moreau's results (Abstr., 1903, ii, 125, 196).
J. C. P.

Combination of a Solvent with the Ions. J. LIVINGSTON R. MORGAN and CLARENCE W. KANOLT (*J. Amer. Chem. Soc.*, 1906, 28, 572—588).—Electrolytic experiments have been made with solutions of silver nitrate in a mixture of ethyl alcohol and water, with a mixture of silver and calcium nitrates in ethyl alcohol and water, and with silver nitrate in a mixture of pyridine and water. The apparatus used in these experiments is described with the aid of a diagram. A platinum cathode and a silver anode were employed. After electrolysis, the solution at each electrode was analysed, and the following results were obtained.

In the electrolysis of solution of silver nitrate in a mixture of ethyl alcohol and water, water migrates with the silver ion, but apparently not more than 1 mol. with each. Lobry de Bruyn (Abstr., 1903, ii, 628) has described similar experiments with silver nitrate dissolved in mixtures of methyl alcohol and water, from which he drew the conclusion that no hydration of the ions occurred. It is pointed out, however, that if he had made corrections for the change in volume due to the change in the amount of silver nitrate in the solution, his results would have indicated a slight hydration of the silver ions. The changes in the composition of the solvent in the electrolysis of a mixture of silver and calcium nitrates in ethyl alcohol and water are probably due to the hydration of the silver ions only; the possible hydration of the calcium ions, however, is not excluded. When a solution of silver nitrate in a mixture of pyridine and water is submitted to electrolysis, a large proportion of the pyridine combines with the silver ions.
E. G.

Relation between the Velocity and the Volume of the Ions of certain Organic Acids and Bases. T. H. LABY and GEORGE A. CARSE (*Proc. Camb. Phil. Soc.*, 1906, 13, 288—295).—The authors compare the velocity of the ion for constant potential gradient (in centimetres per second, per volt, per centimetre) with the cube root of the ion volume. The latter is obtained by subtracting Kopp's value for the atomic volume of hydrogen from the molecular volume of the acid or amine. They find that the product, $\text{velocity} \times \sqrt[3]{\text{volume}}$ is constant for the same series of compounds, so that the velocity is proportional to the linear dimensions of the group, a result similar to that which obtains in the case of motion of small spheres in a viscous liquid.
L. M. J.

Influence of Very Strong Electromagnetic-Fields on the Spark Spectra of (1) Vanadium, and (2) Platinum and Iridium. JOHN E. PURVIS (*Trans. Camb. Phil. Soc.*, 1906, 20, 193—214. Compare *Proc.*, 1905, 21, 241).—The paper describes the effect on a large number of the spectral lines of vanadium, and of the stronger lines of platinum and vanadium, and the values of $d\lambda/\lambda^2$ are given for the constituents of the separated lines.

The values of $d\lambda/\lambda^2$ for many lines are essentially the same, and the method may therefore be regarded as a means of correlating and classifying into groups with the same general properties the spectral lines of elements apart from the alkali metals and the metals of the alkaline earths. Among the strong lines of platinum and iridium which were photographed, there are several which have the same value of $d\lambda/\lambda^2$ for the constituents, and the general appearances both of the constituents and the normal lines are in these cases essentially the same. In some instances, the values of $d\lambda/\lambda^2$ for the several constituents of the same line seem to be simple multiples of each other. Further, the value of $d\lambda/\lambda^2$ for the constituents of some lines is a multiple of the value for the constituents of other lines. J. C. P.

The Correlation between the Variations of the Absorption Bands of a Crystal in a Magnetic Field and the Magnetic Rotatory Polarisation. JEAN BECQUEREL (*Compt. rend.*, 1906, 142, 1144—1146. Compare this vol., ii, 317).—The phenomena of magnetic rotatory polarisation in crystals are intimately connected with the variations of the absorption bands in a magnetic field. When a ray of plane polarised white light falls on a section of xenotime cut normal to the axis and a magnetic field is produced parallel to the incident ray and to the axis of the crystal, the ordinary absorption bands change in intensity, the bands corresponding with the negative electrons increase in intensity and become narrower, whilst those corresponding with the positive electrons diminish in intensity and expand. M. A. W.

Susceptibility of Iron in Colloidal Solution. E. F. BURTON and P. PHILLIPS (*Proc. Camb. Phil. Soc.*, 1906, 13, 260—268).—The experiments of Townsend on the susceptibility of aqueous solutions of iron salts (*Phil. Trans.*, 1896, 533) indicate that, as far as its magnetic properties are concerned, iron exists in four different states: (1) pure iron, (2) ferric iron in salts, (3) ferrous iron in salts, and (4) the acid radicle of salts. As iron is also obtained in colloidal solution, the authors have extended Townsend's work by examining the magnetic properties of a colloidal solution of iron in methyl alcohol, prepared by sparking between two soft iron electrodes beneath the surface of pure cooled methyl alcohol. It was found that the susceptibility of the colloidal iron is about thirteen times that of ferric. The magnetic force was, however, considerably less than that calculated on the supposition that the particles consisted of pure iron, so that either the iron was in a state different from that of iron in other forms of combination or each particle consisted of a core of iron surrounded by a layer of compound, perhaps hydroxide. L. M. J.

Course of Melting-point Curves for Solid Solutions (or Isomorphous Mixtures) in a Special Case. JOHANNES J. VAN LAAR (*Zeit. physikal. Chem.*, 1906, 55, 435—441).—In connection with a point raised by Day and Allen (this vol., ii, 177), the author investigates theoretically the conditions which must be fulfilled in order that the solidus and liquidus curves should approximate very closely to each other and to a straight line. The conclusion reached is that $q_1/T_1 = q_2/T_2$ approximately, and that q_1/T_1 and $(T_1 - T_2)/T_1$ are both small; in which expressions q_1 and q_2 are the latent heats of fusion, T_1 and T_2 are the melting points, of the two constituents. J. C. P.

Abnormal Changes of Melting Point. PAUL ROHLAND (*Chem. Centr.*, 1906, i, 1401; from *Techn. Mitt. Bayr. Gewerbenus. Nürnberg*, 1906, 301—302).—Pure aluminium melts more readily than the impure metal, and the change to the liquid condition does not take place suddenly, an intermediate mixture of solid and liquid being formed. The rise of the melting point may be due to the presence of compounds of aluminium with silicon, iron, lead, or copper, which have higher melting points and cause the mass to sinter, or to the action of the metal itself on air or indifferent gases. Aluminium oxide raises the melting point of pure kaolin. The addition of 10 per cent. or less of magnesium oxide, calcium oxide, potassium oxide, or ferric oxide to silicic acid does not affect the melting point at a temperature of about 1500°, but if a small quantity of aluminium oxide is present, the oxides produce a normal depression. E. W. W.

Variation of Temperature of Fusion with Pressure; Relationship between Absolute Temperature of Fusion and Pressure. D. NEGREANU (*Chem. Centr.*, 1906, i, 116; from *Bull. Soc. Sci. Bucarest*, 1905, 14, 457—471).—From the published data on the influence of pressure on the melting points of different substances, the author concludes that the ratio of the absolute temperature of fusion for two different pressures is constant and independent of the nature of the substance. This empirical relationship is also deduced theoretically from thermodynamic considerations. H. M. D.

Formulæ for the Vapour Pressure of Water, Ice, and Dilute Sulphuric Acid at Low Temperatures. KARL SCHEEL (*Chem. Centr.*, 1906, i, 174; from *Physikal. Zeit.*, 1905, 6, 867—868).—The formula deduced by Hertz for the vapour pressure of mercury is applied to water, the vapour pressure of which is given by $\log p = 23.58682 - 5 \log T - 2933.45/T$. The vapour pressure of ice is similarly given by $\log p = 11.4796 - 0.4 \log T - 2687.4/T$. The agreement with experimental data is very good. Similar formulæ represent the partial pressure of water vapour over dilute sulphuric acid solution in a satisfactory manner. H. M. D.

Vapour Pressure of a Pure Liquid at Constant Temperature. SYDNEY YOUNG (*Sci. Proc. Roy. Dubl. Soc.*, 1906, [ii], 11, 89—104).—The sources of error which must be taken into account in an exact determination of the connection between the vapour pressure

of a liquid and the relative volumes of the liquid and vapour phases are discussed. The author's measurements of a large number of different substances indicate that the vapour pressure is independent of this volume ratio. The variability of the vapour pressure during evaporation or condensation at moderate temperatures must be taken as a proof that the liquid contains air or other impurity. A small amount of decomposition was found by the author to be the cause of variability of the vapour pressure in the case of several liquids examined. In such cases, the variability increases rapidly with the temperature. In the case of the hydrocarbons, about the stability of which there can be no question, the mean percentage difference between the observed pressures corresponding with the lowest and highest volume ratios ($V_{liq.}/V_{vap.}$) was only 0.001.

H. M. D.

Elementary Proof of the Relation between the Vapour Pressures and the Composition of a Binary Mixture. GILBERT N. LEWIS (*J. Amer. Chem. Soc.*, 1906, 28, 569—572).—When a change is made in the composition of a mixture of two liquids, both partial vapour pressures are changed. Duhem (*Compt. rend.*, 1887, 102, 1449) has shown that as one partial pressure decreases, the other increases in accordance with the equation $N(dp/p) + N'(dp'/p') = 0$, where p and p' are the respective partial vapour pressures from a mixture containing N gram-mols. of one substance and N' gram-mols. of the other, and dp and dp' are the changes in p and p' accompanying a slight change in composition.

A simple thermodynamical proof of this law is given, and it is also shown that for a mixture of more than two constituents, $N(dp/p) + N'(dp'/p') + N''(dp''/p'') + \dots = 0$. The equations are true only when the vapours behave like perfect gases, but as this condition is never exactly fulfilled, the equations can only be regarded as approximate.

E. G.

Hydrometer with a Centigram Scale. H. REBENSTORFF (*Chem. Zeit.*, 1906, 30, 569—570).—A modified form of Nicholson's hydrometer, which can be used for rapidly weighing small quantities.

P. H.

Orthobasic Densities of Acetonitrile and Propionitrile to the Critical Point. C. TER-GAZARIAN (*J. Chim. phys.*, 1906, 4, 140—169).—The author has determined the densities of liquid and saturated vapour at temperatures varying from 212° to 271° in the case of acetonitrile, and from 211° to 289° in the case of propionitrile. The method of working, a modification of Young's method, is fully described, as well as the various tests for purity, &c. The results give perfectly linear values for the mean density, and by extrapolation of the line and curve the values for critical temperature and density are found to be 274.7°, 0.2371, and 291.2°, 0.2401 respectively. The ratios of critical to theoretical density are found to be 5.453 and 4.897, high values which indicate considerable polymerisation. The molecular refraction and capillarity also indicate association, but the

liquids obey Trouton's law, and the question of polymerisation is briefly discussed.

L. M. J.

Heterogeneous Equilibrium under Variable Pressures. E. BRINER (*Compt. rend.*, 1906, **142**, 1214—1216).—The effect of variations of pressure on the equilibrium of a system consisting of two gaseous and one solid or liquid phase has been studied by enclosing the gases in a graduated tube surrounded by a vapour jacket of constant temperature, and communicating by means of a tap with a reservoir of mercury, which, in its turn, communicates with a cylinder of liquid carbon dioxide. If p_1 and p_2 represent the partial pressures of the two gases A and B , which form the solid compound A_nB_m , the dissociation pressure of which is represented by π , then for a constant temperature $p_1^n p_2^m = K$; $p_1 = n\pi/(n+m)$; $p_2 = m\pi/(n+m)$; $K = (n^n m^m \pi^{n+m})/(n+m)^{n+m}$, and from these relations, together with the relation $(d \log K)/dT = -q/(KT^2)$, the values of π and the heat q developed can be calculated (compare Isambert, *Abstr.*, 1883, 646, 727).

M. A. W.

Equilibrium in the System Ammonium Sulphate, Lithium Sulphate, and Water. FRANS A. H. SCHREINEMAKERS and D. H. COCHERET (*Chem. Centr.*, 1906, i, 217; from *Chem. Weekblad*, 1905, **2**, 771—778).—The relationships between the double salt, LiNH_4SO_4 , its component salts, and water are described. The solubility of the double salt is nearly independent of the temperature; at -10° , 35.25, and at 70° 36.18 per cent., of the double salt is contained in the saturated solution. At 30° , the solution saturated with double salt and ammonium sulphate contains 39.46 per cent. of ammonium sulphate and 6.50 per cent. of lithium sulphate; the solution saturated with double salt and lithium sulphate, 12.43 and 21.86 per cent. respectively. The cryohydratic temperature of the double salt is -20.7° . When lithium sulphate, $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, is added to a saturated ammonium sulphate solution, successive separation of the following salts takes place: ammonium sulphate, ammonium sulphate and double salt, double salt, double salt and anhydrous lithium sulphate, anhydrous lithium sulphate, anhydrous lithium sulphate and the monohydrate.

H. M. D.

Kinetics of Successive Reactions. FELIX KAUFLEDER (*Zeit. physikal. Chem.*, 1906, **55**, 502—510).—In the course of a study of the hydrolysis by potassium hydroxide of the nitriles of the naphthalenedicarboxylic acids, the author has deduced formulæ representing the course of the change and involving the velocities at which the two nitrile groups are successively removed. The equations may be solved by an approximation method, and it is then found that the formulæ represent with considerable accuracy the course of the hydrolysis, the latter being experimentally followed by the determination of the liberated ammonia. It is found that the velocity of the first reaction is considerably greater than that of the second. The experiments were carried out in amyl alcohol solution at 121° and 126° . J. C. P.

A Method of following the Course of Certain Chemical Actions, and a Period of Induction in the Action of Excess of Water on Monochloroacetic Acid. P. V. BEVAN (*Proc. Camb. Phil. Soc.*, 1906, 13, 269—281).—The paper contains an account of experiments on the velocity of reaction of excess of water on monochloroacetic acid, a unimolecular reaction. The method employed was the determination of the conductivity, instead of the acidimetric method which has been previously employed, and the results show the suitability of the method for such problems. It was found that at the commencement of the reaction there is a period of induction during which the action has not reached its normal velocity. The occurrence of this period of induction indicates that the reaction must not be regarded as a simple unimolecular reaction, and is explained if it is considered that the first stage of the action is the association of water and monochloroacetic acid to form an unstable compound which breaks down into glycollic and hydrochloric acids. L. M. J.

Formation of Acid Salts in Alkaline Solution. ALFRED BENRATH (*J. pr. Chem.*, 1906, [ii], 73, 390—392).—Whilst in aqueous solution the neutralisation of a polybasic acid by an alkali hydroxide takes place immediately, in alcoholic solution, in consequence of the diminished ionic dissociation, the stages in the neutralisation are differentiated sufficiently to allow often of the isolation of intermediate acid salts. The action of 1 mol. of an alkali ethoxide on tartaric acid in alcoholic solution leads to the formation of the gelatinous acid salt, which gradually becomes crystalline, but an excess of the alkali ethoxide leads to the formation of a mixture of the acid and normal tartrates, the complete conversion of the acid into the normal salt taking place only on prolonged contact of the precipitate with the alkaline alcoholic solution. When 1 gram of sodium and 3.3 grams of tartaric acid dissolved in equal volumes of alcohol are stirred together for five minutes, the proportion of the acid salt in the precipitate is greatest (76 per cent.) when concentrated (40 c.c.), least (19 per cent.) when dilute solutions (100 c.c.) are used at low temperatures (0—10°); variations in the dilution (40—100 c.c.) have little influence on the composition of the precipitate (50.5—49 per cent. of the acid salt) at 100°. The c.c. given are the total volumes of alcohol in the mixtures. Low temperatures and high dilutions are favourable to the prolonged existence of the gelatinous form of the acid salt, which reacts with the excess of alkali ethoxide more readily than does the crystalline form.

Similar results were obtained with sulphuric and phosphoric acids, but in consequence of the great reactivity of sodium hydrogen sulphate in alcoholic solution, the complete neutralisation of sulphuric acid takes place more rapidly. G. Y.

Autocatalysis and Decomposition in a Photochemical System. BÉLA SZILARD (*Compt. rend.*, 1906, 142, 1212—1214. Compare Stubenrauch, *Abstr.*, 1899, i, 398; Bougault, *Abstr.*, 1899, i, 1; Kremers and Koske, *Abstr.*, 1899, i, 397; Schuyten, *Abstr.*, 1901, i, 3; Hardy and Willcock, *Abstr.*, 1903, ii, 622; van Aubel, *Abstr.*,

1905, i, 1).—The decomposition of iodoform in chloroform, ether, alcohol, or carbon disulphide solution in the presence of oxygen is an autocatalytic reaction, the velocity of which is represented by the relation $q = (Q - a)^{-1} = 1 - e^{-bt}$, where q is the quantity of iodine liberated in time t (in days), Q is the amount of iodine (as CHI_3) in milligrams in one cubic centimetre of the solution; $Q - a$ the limit of decomposition of the system, and b a constant which is a function of the temperature, the concentration, and the purity of the materials employed.

The action of light in promoting the decomposition of iodoform solutions is also represented by a similar logarithmic curve.

M. A. W.

Anticatalytic Action of Water. GEORG BREDIG and W. FRAENKEL (*Ber.*, 1906, 39, 1756—1760. Compare Abstr., 1905, ii, 692; Goldschmidt and Sunde, this vol., ii, 219).—The velocity constant of the reaction $\text{N}_2 \cdot \text{CH} \cdot \text{CO}_2 \text{Et} + \text{EtOH} = \text{OEt} \cdot \text{CH}_2 \cdot \text{CO}_2 \text{Et} + \text{N}_2$, with picric acid as catalyst, is influenced by traces of water, 0.18 per cent. lowering it by about 22 per cent. under the conditions quoted by the authors. In any one experiment, the velocity constant diminishes with time owing to a secondary action between the picric acid and the ethyl diazo-acetate (Curtius, *J. pr. Chem.*, 1888, [ii], 38, 396). The velocity constant in alcoholic solution is not proportional to the concentration of the picric acid.

[With DAVID M. LIGHTY.]—The retarding influence of water on the decomposition of oxalic acid by sulphuric acid has been examined. The presence of 0.05 per cent. of water in about 100 per cent. sulphuric acid increases the time required for a given amount of decomposition from fifty minutes to three hours. With sulphuric acid containing 1 per cent. of sulphur trioxide, the reaction at 0° is too rapid for measurement; with 1 per cent. of water, the system must be heated at 50° for one hour before a measurable reaction takes place.

In conclusion, Bredig denies that he regards hydrogen cyanide as an invariable anti-catalyst (compare Loevenhart, this vol., ii, 153).

C. S.

Catalysis and Electromotive Force. I. ALDO BRINGHENTI (*Gazzetta*, 1906, 36, i, 187—215).—The catalytic power of platinum is exercised on solutions of sodium methoxide, ethoxide, and *n*-propoxide in the corresponding alcohols and on the latter themselves in solutions which are rendered alkaline with sodium hydroxide, and which probably contain a certain amount of alkoxide. The products formed are evidently acid in nature, since they alter the alkalinity of the solutions, thus rendering it possible to follow the course of the catalysis. It is quite possible that, under these conditions, the alcohols undergo complete transformation into the corresponding acids, methyl alcohol giving formates, and so on. The catalysing action of the platinum depends on the quantity of the catalyst and on the concentration of the alkoxide. No exact proportionality exists between these magnitudes, but the catalysis diminishes with the concentration of the catalyst as well as with that of the alkoxide. The amount of catalytic action falls

considerably on passing from sodium methoxide to ethoxide, and, to a less extent, in passing from the ethoxide to the propoxide. Methyl-alcoholic solutions of sodium hydroxide also undergo catalysis by means of platinum, although in a much less degree than the alkoxides. Platinum black, prepared by the method given by Loew (*Abstr.*, 1890, 453), exerts a much greater catalytic action than platinum obtained by reduction with zinc, probably owing, firstly, to it being more finely subdivided and so offering a larger active surface, and, secondly, to its content of true organic compounds of platinum (Loew, *loc. cit.*). Palladium behaves similarly to platinum, and a certain catalytic activity is also exhibited by silver and by the oxides of nickel, iron, cobalt, and manganese. Of the solvents used, water is the one exercising the greatest retarding action on the catalysis, probably owing to its hydrolysing effect on the alkoxides.

On immersing a large electrode of platinised platinum and a small one of smooth platinum in an alcoholic solution of the corresponding sodium alkoxide, an electro-motive force is observed, which is not, however, very constant, and varies with the time at which the circuit is closed and with the surface of the electrodes; the measurement of the polarisation is hence rendered difficult, the voltage-intensity curves being somewhat irregular. The effect of platinum black on the reduction potential of methyl alcohol is also produced by formaldehyde, and as the latter can be formed by the catalytic action of the platinum on the alcohol, it is to the production of aldehyde that the author attributes the action of the platinum. The results are discussed theoretically.

T. H. P.

Oxidising Catalytic Agents; Generalisation of the Lamp without Flame. CAMILLE MATIGNON and RENÉ TRANNOY (*Compt. rend.*, 1906, 142, 1210—1211).—The oxides of iron, nickel, cobalt, chromium, copper, manganese, cerium, or silver are able to act catalytically as active oxidising agents under certain conditions, thus if a thread of asbestos impregnated with a solution of the nitrate of one of these metals is ignited, it becomes coated with the metallic oxide in a state capable of realising the phenomenon of the lamp without a flame, for on plunging such a thread into a vessel containing ether vapour, it becomes incandescent and the ether burns with the formation of acetaldehyde; similar results are obtained when the ether is replaced by other organic compounds at such a temperature that the vapour pressure is appreciable. The catalytic action of metallic copper in inducing the combustion of ammonia and other volatile primary amines is shown by placing a spiral of copper heated to redness just above the surface of the concentrated solution of the amine; the spiral becomes incandescent, and when the wire is thin it frequently fuses.

M. A. W.

Numerical Studies on the Equation of Fluids. Determination of the Constants α and b . LOUIS FRIDERICH (*J. Chim. phys.*, 1906, 4, 123—139).—From van der Waals' equation, on the assumption of three equal roots of the cubic equation in v at the critical temperature, certain deductions regarding α and b are obtained, but these are

not in accord with experiment. For example, $b = RT_c/8p_c$ and $b = v_c/3$, but the values so obtained are generally widely divergent. The author investigates the equation, assuming, however, only two equal roots. The calculation is simple and leads to

$$b_c = -\frac{1}{2}\left(\frac{RT_c}{p_c} - 2v_c\right) + \sqrt{\frac{1}{4}\left(\frac{RT_c}{p_c} - 2v_c\right)^2 + \left(\frac{RT_c}{2p_cv_c} - 1\right)v_c^2}.$$

The values of b_c are calculated, from data due to Young, for a large number of compounds, and the ratios v_c/b are found. With the exception of liquids regarded as associated (such as acetic acid, methyl alcohol) the values all lie between 2.422 and 2.483, the mean value being 2.442. Assuming this mean value, the ratio of theoretical and actual critical density is obtained as 3.85, a result in accord with experiment. The values of a_c for the compounds are also calculated and a table given. The values of a at various temperatures are calculated in the case of isopentane on the assumption that a and b are independent of volume, and from these are derived the values of dp/dt , which show fair accord with the experimental values; but the accord does not allow of the statement that a and b are independent of volume. Other methods of calculation of a are used in which this assumption is not made, and in all cases the values of a , however calculated, are decreasing functions of the temperature.

L. M. J.

Ionic Size in Relation to the Physical Properties of Aqueous Solutions. WILLIAM R. BOUSFIELD (*Phil. Trans.*, 1906, A, 206, 101—159. Compare Abstr., 1905, ii, 369).—If the ions of electrolytes are combined with water, as is very generally supposed, then the size of the ions will be subject to change with dilution. In following up this line, the author has arrived at the following relation between the average radius r of an ion and the dilution of the solution, $r = r_\infty / (1 + Bh^{-\frac{2}{3}})^{-1}$, where h is the hydration. This function r the author proposes to designate by the term "radion." The foregoing theoretical result could be tested only by considering how the hypothesis as to the changing sizes of the ions owing to changes in the amount of combination with water could be related rationally to the various physical properties of aqueous solutions. In carrying out this test, the electrolytes used were sodium and potassium chlorides.

A priori, it was to be expected that the Hittorf transference numbers and the viscosities of the solutions would depend merely on the linear dimensions of the ions, whilst the densities of the solutions and the variations of effective molecular freezing-point depression and refractive power would depend on the amounts of combined water, and therefore on the cubes of the ionic dimensions. These expectations have been justified, not merely in a qualitative manner, but with considerable numerical accuracy. The Hittorf numbers, the densities, the effective molecular freezing-point depressions, and the equivalent refractive power within the limits of experimental error may be expressed as simple functions of the radions; the viscosities may be expressed not merely as a function of the radions of the solute, but also on the extended conception of the radion as being simply proportional to the average molecular radius of the whole solution. New

relations, independent of the hypothesis, have been discovered, namely: (1) the Hittorf migration numbers are a linear function of $(B + h^3)^{-1}$; (2) the effective molecular freezing-point depression and the equivalent refractive power are linear functions of the solution volume.

In an appendix, the author gives reasons for supposing that van't Hoff's law (index = $\frac{2}{3}$) is an accurate law for certain binary electrolytes with univalent ions.

J. C. P.

Iodine as a Cryoscopic Solvent. J. TIMMERMANS (*J. Chim. phys.*, 1906, 4, 170—173).—It is found that iodine is easy to manipulate as a cryoscopic solvent; its cryoscopic constant calculated from its latent heat of fusion is 252.13, and stannic iodide is found to give values 254.25, 249.60, 255.53, and 240.71. The author uses the value 252, and finds that potassium iodide and mercuric iodide both give high values for the molecular weight, indicating polymerisation.

L. M. J.

Colloidal Salts. II. Formation of Hydrosols by the Interaction of Ions. ALFRED LOTTERMOSER (*J. pr. Chem.*, 1906, [ii], 73, 374—382. Compare Abstr., 1905, ii, 586).—If the liquid hydrosol of silver iodide is formed by adding silver nitrate to potassium iodide in aqueous solution, the presence of a certain amount of iodine in the ionic state is necessary to its existence; thus, if 50 c.c. of $N/10$ silver nitrate are added to 50 c.c. of $N/10$ potassium iodide, silver iodide is precipitated in the "molecular" state completely during the addition of the last 0.5 c.c. The precipitate is free from silver nitrate (compare Köthner and Aeuer, Abstr., 1905, ii, 81). It is because of the presence of iodine anions in the hydrosol and of potassium cations in the solution prepared in this manner that on electrolysis of the liquid hydrosol the colloidal silver iodide accumulates at the anode, whilst the contrary is the case when the hydrosol contains silver cations and the solution NO_3 anions. This may be connected with the fact that in the double salt, KI, AgI , the anion is AgI'_2 , whilst $\text{Ag}_2\text{I}'$ is the cation of the salt, $\text{AgI}, \text{AgNO}_3$.

Rapid addition of an excess of silver nitrate solution to the liquid hydrosol of silver iodide causes only a slight precipitation of "molecular" silver iodide, but the precipitation is complete if $N/10$ silver nitrate is added carefully in slight excess. In this case, the hydrogel is formed by the reaction of silver ions with the iodine ions in the hydrosol, and therefore is of greater weight than that obtained by the action of nitric acid on the same volume of the liquid hydrosol.

It is probable that other hydrosols behave in a similar manner.

G. Y.

Adsorption of Dissolved Substances. PERCY N. EVANS (*J. Physical Chem.* 1906, 10, 290—298).—The paper contains briefly the results of a number of experiments made by the author with his students on adsorption, chiefly by filter paper. In the case of hydrochloric acid, filter paper was found to remove about 0.0006 to 0.0007 gram per gram of paper from dilute solutions of the acid. The

adsorption was less (0.00015) in the case of sodium chloride and of potassium chloride. No adsorption was found with barium chloride, but with copper sulphate the adsorption increased markedly on dilution, reaching a maximum for a 0.08*N* solution. The actual numbers vary with the filter paper employed, probably owing to differences in the extent of the surface. The values for the adsorption by silica for copper sulphate were also found, and these also indicate a maximum for solution of about 0.02*N*.
L. M. J.

Absorption Compounds. IX. Difference between Hydrates and Hydrogels and the Modifications of Hydrogels (Zirconic and Metazirconic Acids). JACOBUS M. VAN BEMMELEN (*Zeit. anorg. Chem.*, 1906, **49**, 125—147. Compare Abstr., 1904, ii, 18; 1905, ii, 461; Ruer, Abstr., 1905, ii, 256).—The author has recently expressed the view that the metazirconic acid described by Ruer (*loc. cit.*) is not an isomeride of zirconic acid in the ordinary sense, but a colloidal modification, a hydrogel. The present paper contains an account of the properties of zirconic and metazirconic acids, more particularly as regards behaviour on dehydration and absorptive power for moisture.

Zirconic acid, prepared by the action of excess of ammonia on zirconium chloride, behaves as a hydrogel up to 130°; in other words, the proportion of water present varies continuously with the temperature and the pressure of aqueous vapour. The dehydration is not completely reversible, but the acid still possesses a limited absorptive power. Between 140° and 200°, the proportion of water is constant, corresponding with the formula $\text{ZrO}_2 \cdot \text{H}_2\text{O}$; above the latter temperature, the proportion becomes less and the absorptive power decreases after each heating. It does not follow, however, from the constancy of composition between the above limits that a definite hydrate exists, since under these conditions it has still absorptive power.

Modified zirconic acid (metazirconic acid), prepared from the oxychloride by Ruer's method, is at first a hydrosol, which, on continued boiling with water, becomes a hydrogel. It contains less water and has a smaller absorptive power than the ordinary acid, and the absorptive power is smaller the longer the boiling is continued; contrary to Ruer's contention, there is no evidence of the formation of a definite hydrate on dehydration.

As regards the general question of the difference between hydrates and hydrogels or hydrosols, the author distinguishes three possible cases: (1) chemical hydrates, crystalline, dehydration proceeds in stages and is reversible; (2) chemical hydrates, crystalline, dehydration irreversible owing to change of structure; (3) oxides or hydroxides in colloidal form; the composition depends on colloidal structure and alters continuously with pressure and temperature.
G. S.

Structure of "Apparently Living" Crystals. OTTO LEHMANN (*Ann. Physik*, 1906, [iv], **20**, 63—76).—The crystals referred to in the title are fluid crystals, such as those of ethyl *p*-azoxycinnamate (Vorländer, this vol., i, 317), the behaviour of which resembles in some

points that of living organisms. They lack, however, certain other essential characteristics of living organisms.

In the present paper, the author endeavours to draw a picture of the structure and to interpret the behaviour of these fluid crystals. Emphasis is laid on the distinction between this and other cases in which inorganic matter seems to possess some of the characteristics of living organisms.

J. C. P.

Continuity of the States of Aggregation; Fluid Crystals. OTTO LEHMANN (*Ann. Physik*, 1906, [iv], 20, 77—86).—The existence of fluid crystals cannot be reconciled with the theory of the continuity of the states of aggregation. The author considers that this theory must be given up, and shows that, if the existence of molecules is assumed at all, the molecules of a substance must be different in the different states of aggregation. Further, the polymorphic modifications of a substance differ not only in the arrangement of the molecules, but also in the character of the molecules themselves. The chemist assumes that when two substances have the same molecular weight and exhibit the same chemical behaviour, they must consist of the same molecules. The author, on the other hand, points out that there must be a kind of molecular difference which is not discoverable by chemical methods.

J. C. P.

Number of Corpuscles in an Atom. JOSEPH J. THOMSON (*Phil. Mag.*, 1906, [vi], 11, 769—781).—The author considers three methods of determining the number of corpuscles in an atom of an elementary substance, methods based on (1) the dispersion of light by gases, (2) the scattering of Röntgen radiation by gases, (3) the absorption of β -rays. All the methods lead to the conclusion that the number of corpuscles in an atom is of the same order as the atomic weight of the substance, and two of the methods show further that the ratio of the number of corpuscles in the atom to the atomic weight of the element is the same for all elements. Further investigation, perhaps, is necessary before it can be stated with certainty that the number of corpuscles in the atom is equal to the atomic weight.

J. C. P.

The Chemical Elements. A New Classification. GEO. WOODIWISS (*Chem. News*, 1906, 93, 214—215).—The author arranges the elements in the order of their atomic weights and divides the series into periods according to the specific gravities of the elements in the solid (or liquid) state at 0°.

H. M. D.

Ultra-microscope and its Application to Chemistry. LEONOR MICHAELIS (*Zeit. angew. Chem.*, 1906, 19, 948—953).—The use of the ultra-microscope is not to produce an exact image of any given object, but rather to make it visible as a luminous spot against a dark background. If a beam of light is allowed to pass through ruby glass, coloured by means of gold, it renders the particles of gold luminous, and on examining the beam of light with a microscope held at right angles to its direction the gold particles (although too minute to be shown by the highest powers of an ordinary microscope) appear as a

number of glistening points. By counting the number of particles in a certain area and estimating the amount of gold by analysis, the size of the particles was found to vary from 6 $\mu\mu$ to 30 or 40 $\mu\mu$. The shape of the particles could not be seen, but from their optical behaviour they appeared most likely to be elongated. A dilute aqueous solution of thionin containing a little sodium hydroxide examined in the same way was also found to contain small suspended particles, whereas a solution containing no alkali was found to be homogeneous, thus showing that solutions of colouring matters are partly true solutions and partly fine suspensions. The same remarks apply to solutions of proteids in water. Although the ultra-microscope cannot be used as a substitute for the ordinary microscope, owing to the entire absence of definition in the images, it may, nevertheless, be used for determining whether a solution is a true solution or whether it contains minute suspended particles too small to be detected by other means. P. H.

Receiver for Vacuum Distillations rendered Air-tight by Mercury. LEO UBBELOHDE (*Zeit. angew. Chem.*, 1906, 19, 757—758).—The receiver is of the same form as Brühl's apparatus. For the details of the way in which the joints are rendered air-tight, the original must be consulted. J. C. P.

Apparatus. I. Melting-point Tube Holder. II. Suction Funnel with Stretched Filter. WILHELM LENZ (*Chem. Centr.*, 1906, i, 169; from *Ber. deut. pharm. Ges.*, 1905, 15, 358—361).—I. The usual rubber ring is replaced by a spiral spring which is stretched over a piece of thin sheet metal bent into the form of a ring through which the thermometer passes. Three grooves on the inside of the ring permit of the attachment of the melting-point tubes.

II. The funnel consists of two parts, the upper portion being screwed into the lower, which carries a perforated brass plate, between which and a superposed brass ring the filter is placed. When the two parts are screwed together, the filter is firmly fixed in position by the pressure on the brass ring. H. M. D.

New Shortened Barometer with Reproducible Vacuum, combined with Two Forms of the Compact Pressure Gauge. LEO UBBELOHDE (*Zeit. angew. Chem.*, 1906, 19, 756—757. Compare following abstract).—The barometer consists of a tube bent twice upon itself. This tube is set upright and filled with mercury; by adjusting the outside pressure, the mercury column breaks away on both sides of the top bend, leaving an absolute vacuum. J. C. P.

Automatic Shortened Mercury Pump combined with a Compact Apparatus for Measuring High Vacua. LEO UBBELOHDE (*Zeit. angew. Chem.*, 1906, 19, 753—756).—The device adopted is to connect the space above the mercury in the reservoir with the water pump. The apparatus for measuring the high vacua is a modified McLeod gauge. For diagrams and details the original must be consulted. J. C. P.

Siepermann-Fudickar Water Pump. A. VON IHERING (*Chem. Zeit.*, 1906, 30, 516—517).—The pump, which can be used either as a vacuum or a compression pump, is worked by a very slowly descending stream of water. P. H.

New Gas Generating Apparatus. W. SCHMIDT & CIE. (*Chem. Zeit.*, 1906, 30, 474—475).—The apparatus consists of a large Wolff's bottle with three openings; the side ones are small and are designed for a safety funnel and a delivery tube respectively, whilst the centre opening is fitted with a large cylindrical funnel for the acid and is sufficiently wide to admit of the passage through it of a special holder for the solid reagent. Owing to the design of the latter, the bubbles of gas as they escape effect a thorough circulation of the acid, with the result that a very brisk evolution of gas ensues. The apparatus can be charged with five holders, each containing 600 grams of ferrous sulphide, and if filled with 10 litres of commercial hydrochloric acid (3 volumes of acid to 1 of water) will supply 10 litres of hydrogen sulphide per minute. The apparatus can also be obtained double this size.

P. H.

Shaking Apparatus fitted with a Gas Delivery Tube and a Temperature Regulator. R. KEMPF (*Chem. Zeit.*, 1906, 30, 475).—The apparatus consists of a glass cylinder through which a spiral worm passes. By allowing cooled brine or a hot liquid to circulate through this, the temperature within the cylinder can be kept more or less constant between the limits of 0° and 100°. A tube projecting vertically from the side of the cylinder enables any gaseous products of the reaction to be collected, and by placing the whole apparatus in a shaking apparatus the contents can be thoroughly agitated, the spiral worm acting as a means of breaking up the contained liquid. P. H.

Combined Suction and Washing Flask with Three-way Cock and Tube reaching to the Bottom. SCHUSTER STEINEBACH (*Chem. Centr.*, 1906, i, 1473; from *Zeit. chem. Apparatenkunde*, 1, 293).—The apparatus consists of a conical flask, to the top of which a glass funnel is fitted by means of a ground glass joint. A short glass tube with a three-way cock is sealed to the flask on one side of the funnel, whilst on the opposite side a glass tube with a simple cock is similarly attached; the tube, however, in this case passes into the flask and reaches nearly to the bottom. For the purpose of filtering, the latter is connected with the pump by means of an ordinary suction bottle. When the filtrate has reached a certain depth, air is allowed to enter the flask by opening the three-way cock and the liquid driven over into the suction bottle. The speed of filtration is readily regulated by means of the cocks, and the return of water from the pump prevented.

The apparatus may also be used as a washing bottle by replacing the funnel by a glass tube fitted in a rubber bung. E. W. W.

Inorganic Chemistry.

Combination of Hydrogen and Oxygen in Contact with Hot Surfaces. WILLIAM A. BONE and RICHARD V. WHEELER (*Phil. Trans.*, 1906, A, 206, 1—67).—An apparatus is described whereby it is possible to circulate a given mixture of hydrogen and oxygen at a given rate through a combustion tube packed with the catalytic material, a manometer attached to the apparatus indicating the velocity with which the two gases combine.

The first catalytic substance chosen was porous porcelain, and it appears from the authors' work that the rate of steam formation is not governed either by the order of the reaction (see Bodenstein, *Abstr.*, 1904, ii, 245) or by diffusion factors simply (see Nernst, *Abstr.*, 1904, ii, 315). The theory of a rapidly alternating series of oxidations and reductions of the catalysing surface is inadmissible, and the experimental evidence strongly supports the view that the catalytic action of porcelain is primarily due to the condensation or occlusion of one, and possibly both, of the reacting gases on its surface. The fact that when one or other of the gases is in excess the rate of combination is proportional to the partial pressure of the hydrogen, and that the material absorbs hydrogen at a red heat, indicates that occluded hydrogen is an all-important factor in the process. Occluded oxygen also may exercise an accelerating influence, but whilst excess of hydrogen produces a continuous acceleration throughout a given experiment, any acceleration due to oxygen is manifested only during the initial stages. The view of the catalytic process suggested by these facts is as follows. Porous porcelain occludes or condenses both hydrogen and oxygen at rates which depend to some extent on the physical condition and past history of the surface. In general, however, whereas in the case of oxygen the process is extremely rapid and the surface layer is soon saturated, the occlusion of hydrogen is slower, and the limit of saturation much higher. Combination between the occluded gases occurs at a rate either comparable with, or somewhat faster than, the rate at which the film of occluded oxygen is renewed, but considerably faster than the rate of occlusion of hydrogen.

When calcined magnesite is taken as the catalytic surface, it is found that (1) with normal electrolytic gas the rate of combination is proportional to the pressure of the dry gas, (2) when excess of either gas is present, the rate of combination is determined mainly by the partial pressure of the hydrogen, (3) the catalysing power of the material is greatly stimulated by hydrogen, but diminished by oxygen. The material at a red heat absorbs hydrogen, but not oxygen, and it may be concluded that its catalytic action is due to its power of occluding hydrogen.

Experiments with silver, gold, platinum, and nickel as catalytic substances show that the catalytic action in each case is primarily due to an association of the surface with hydrogen, in the case of silver probably to the formation of an unstable hydride, in the other three cases to an occlusion of the gas. Statements (1) and (3) for calcined

magnesite apply also in the case of these four metals. When an excess of either gas is present, the rate of combination is nearly proportional to the partial pressure of the hydrogen, although in the case of silver this only holds good up to a point of "maximum hydrogenation" of the surface. The evidence in favour of the occlusion theory is particularly strong in the case of nickel, where the normal condition of activity can be reduced to almost vanishing point by prolonged exhaustion at a comparatively low temperature. The subsequent recovery of activity can be demonstrated by circulating successive charges of electrolytic gas over the surface under conditions which entirely preclude any chemical action of either gas on the metal.

The authors have examined also the action of easily reducible oxides, and chose for this purpose calcined spathic iron ore, copper oxide, and nickel oxide. Suitable temperatures, at which the catalytic combination of the gases would proceed with fair velocity, without the surface itself undergoing any permanent change, were found to be 200° in the case of calcined spathic iron ore and copper oxide, and 160° in the case of nickel oxide. So far as the catalytic action of nickel oxide and calcined spathic iron ore is concerned, it is found (1) that the rate of combination with normal electrolytic gas is always proportional to the pressure of the dry gas, and far exceeds either the rate of reduction of the catalysing surface by hydrogen or its rate of re-oxidation by oxygen; (2) that when the gases are not present in combining proportions, the rate of combination is solely determined by the partial pressure of the hydrogen. It appears that the catalytic action in these cases also is due to a physical condensation of the hydrogen at the surface of the oxide, the hydrogen being thereby rendered active. The behaviour of copper oxide also is incompatible with any purely chemical explanation of the catalytic process. The process in this case appears to involve the condensation of a film of "active" oxygen on the surface, this film actually protecting the catalysing oxide from the attacks of the hydrogen. At low pressures, the film becomes too thin to ensure complete protection, and the formation of steam is accelerated by reason of hydrogen penetrating to the oxide and reducing it. In conformity with this idea, the rate of steam formation when the gases are not present in combining proportions is found to be proportional to the partial pressure of the oxygen.

J. C. P.

Changes in the Properties of Elements, especially Chlorine.

RUDOLF FABINYI and LUDWIG FÖRSTER (*Chem. Centr.*, 1906, i, 636; from *Physikal. Zeit.*, 1906, 7, 63—68).—When sulphuric acid is allowed to drop on a mixture of potassium dichromate and sodium chloride, chlorine I is obtained, which differs from chlorine II, obtained by adding a solution of sodium chloride to a mixture of potassium dichromate and sulphuric acid, the temperature and apparatus in both cases being identical. Chlorine I is light greenish-yellow, and its solution in water is light green, whilst chlorine II is deep yellowish-green and forms a solution which has a dark green tone. A saturated solution of chlorine II contains rather less chlorine than a similarly saturated solution of chlorine I. A solution of chlorine II in water is converted into hydrochloric acid rather more rapidly than one of

chlorine I. Chlorine II was proved to be free from chromyl chloride. These differences may possibly be accounted for by assuming that the chlorine atoms in the two cases possess different numbers of electrons.

P. H.

Reaction between Chloric Acid and Hydrochloric Acid.

ROBERT LUTHER and F. H. MACDOUGALL (*Zeit. physikal. Chem.*, 1906, 55, 477—484).—The reaction between chloric and hydrochloric acids (at 75°) is markedly retarded by chlorine, and the reaction velocity is, *ceteris paribus*, inversely proportional to the square root of the chlorine concentration. It is very probable that the process involves the equilibrium $\text{ClO}_3' + 2\text{H}' + \text{Cl}' \rightleftharpoons \text{ClO}_2 + \frac{1}{2}\text{Cl}_2 + \text{H}_2\text{O}$. It follows from the authors' experiments that Sand's views on the mechanism of this reaction (*Abstr.*, 1905, ii, 156) are out of harmony with the actual facts.

J. C. P.

Reaction between Potassium Persulphate and Iodide and Bromide in Aqueous Solutions, and its Application in Medicine. BERNHARD MERK (*Chem. Centr.*, 1906, i, 397; from *Pharm. Zeit.*, 50, 1022—1023).—Potassium persulphate is hydrolysed by water into potassium hydrogen sulphate and the corresponding persulphate. These yield with potassium iodide and bromide, hydriodic and hypiodous acids and hydrobromic and hypobromous acids respectively (the latter being at first only formed sparingly and not readily until the iodine has separated completely); the hydriodic and hypiodous acids then yield free iodine, the hydrobromic and hypobromous acids free bromine, the two halogens in turn yielding bromine iodide. It is possible that this reaction may prove useful in the treatment of diseases of the bladder.

L. DE K.

Electrolytic Formation of Thiosulphates.

MARIO G. LEVI and M. VOGHERA (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 363—369. Compare this vol., ii, 81 and 348).—The yield of thiosulphate is found to be increased if the cathodic sulphide solution is replaced by a solution of polysulphides. The other conditions most favourable to the change represented by $\text{SO}_3'' + \text{S}'' + 2\oplus = \text{S}_2\text{O}_3''$ are the use of a platinised platinum anode, a low anodic current density, and a concentrated sulphite solution maintained as faintly alkaline as possible with alkali carbonate.

T. H. P.

Action of Organic Reducing Agents on Selenious Acid.

WILLIAM OECHSNER DE CONINCK and CHAUVENET (*Bull. Acad. roy. Belg.*, 1906, 51—52. Compare this vol., ii, 81, 279).—Formaldehyde, paraldehyde, lævulose, and dextrose reduce selenious acid, forming a red, amorphous selenium, which at the atmospheric temperature is insoluble in carbon disulphide. When the reduction is effected at 100°, a small quantity of black selenium is also produced.

T. A. H.

Atomic Weight of Tellurium.

ALEXANDER GUTBIER and B. GOSSNER (*Chem. Centr.*, 1906, i, 635—636; from *Sitzungsber. Phys.-Med. Soc. Erlangen*, 1906, 37, 270—311. Compare *Abstr.*, 1906, ii,

81).—A summary, with references, of all atomic weight determinations of tellurium hitherto published. The following additional details with regard to the two varieties of telluric acid are also given; the α -modification, which forms cubical singly refracting octahedra of sp. gr. 3.035, separates from a nitric acid solution together with a small amount of the β -variety, but in very concentrated solutions none of the latter form is deposited. The β -modification of sp. gr. 3.071 is deposited from warm nitric acid solution in clear, monoclinic, prismatic crystals, $a:b:c = 0.6104:1:0.5206$; $\beta = 104^\circ 30'$. The conversion of the α into the β variety has been observed, but not the reverse change. P. H.

Action of the Silent Electric Discharge on Ammonia and Oxygen. ROBERT POHL (*Chem. Centr.*, 1906, i, 814; from *Ber. phys. Ges.*, 4, 10—15).—Experiments have been made by passing a silent discharge at 5000—10,000 volts through an ozonising tube containing ammonia or oxygen. In the former case, the presence of traces of moisture was found to inhibit the decomposition of the gas to a considerable extent, and the efficiency also became less when the current density was increased; increase of the *E.M.F.* employed, of the pressure of the gas, or of the thickness of the layer traversed had, however, an opposite effect.

When pure oxygen or the oxygen of the air was ozonised, the maximum efficiency was obtained by using an *E.M.F.* of about 6500 volts. E. W. W.

Formation of Nitric Oxide at High Temperatures. WALTHER NERNST (*Zeit. anorg. Chem.*, 1906, 49, 213—228).—A more detailed account of work already published (compare Abstr., 1905, ii, 24, 444; Finckh, Abstr., 1905, ii, 444). G. S.

Velocity of Decomposition of Nitric Oxide and its Dependence on the Temperature. KARL JELLINEK (*Zeit. anorg. Chem.*, 1906, 49, 229—276. Compare preceding abstract).—The rate of decomposition of oxide at high temperatures was measured by Nernst's method (Abstr., 1905, ii, 24). Owing to the powerful catalytic action of platinum on the reaction at relatively low temperatures, the measurements between 689° and 1347° were made in porcelain tubes; under these circumstances the action is bimolecular, and its velocity is practically unaffected by the presence of moisture. From 1347 — 1605° , the experiments were made in a platinum vessel, and final measurements at 1750° in an iridium vessel. From 1347 — 1508° , the reaction is approximately unimolecular, and what is being measured is probably the rate of diffusion of the gas to the platinum surface (compare Nernst, Abstr., 1904, ii, 315), but at higher temperatures the catalytic effect is relatively much less and the reaction again becomes approximately bimolecular.

From 689° to 1347° , the relation between velocity constants and temperature is given by the simple equation $\log k = A/T + B$, where T is the absolute temperature and A and B are constants; in other words, the reaction velocity is increased in the same ratio for equal increments of temperature throughout this range, and is approximately

doubled by a rise of 50° . The same equation holds approximately at 1600 — 1750° , when the catalytic action of platinum and iridium falls off. The agreement between the observed constants and those calculated from the above equation is only moderate, and somewhat better results are obtained by adding the term $-C/T$ to the right-hand side of the equation—a correction which becomes negligible at high temperatures. The van't Hoff-Arrhenius equation, $\log k = -A/T + B$, which holds for so many reactions at lower temperatures, does not apply in this case.

If the period during which the gas remains at the temperature of the explosion when mixtures of electrolytic gas and air are fired could be determined, velocity measurements could be carried out at much higher temperatures, but, as this cannot at present be done satisfactorily, the reaction velocities at the temperature of the explosion were calculated by extrapolation, and from Finckh's determinations of the amounts of nitric oxide produced under these conditions (compare Abstr., 1905, ii 444) the times of heating were calculated; they are of the order $1/10,000$ second at 2600 — 2700° under atmospheric pressure.

G. S.

Oxides of Nitrogen and the Lead-chamber Process. GEORG LUNGE and ERNST BERL (*Zeit. angew. Chem.*, 1906, 19, 807—819, 857—869, 881—894).—The paper is a reply to Raschig's refutations of the present authors' theory of the lead-chamber process (compare Abstr., 1905, ii, 23, 700). By working through a number of their own analytical methods, they have been able to confirm their trustworthiness and to disprove Raschig's statement that sulphuric acid reacts with nitrogen peroxide to form an appreciable quantity of nitrous oxide and nitrogen. Raschig's view that nitric oxide is converted into nitrogen peroxide through the intermediate step of the trioxide is incorrect, and the equation $2\text{NO} + \text{O}_2 = \text{N}_2\text{O}_4$ still holds good. Following on a detailed discussion of some of their more recently obtained experimental results, the authors summarise in detail their objections to Raschig's propositions. As a result of this, Lunge's theory of the lead-chamber process is slightly modified, for, in place of the original equation, $2\text{SO}_2 + \text{NO} + \text{NO}_2 + \text{O}_2 + \text{H}_2\text{O} = 2\text{SO}_5\text{NH}$, an intermediate step (i) is now inserted, corresponding to the formation of sulpho-nitronic acid, SO_5NH_2 , which is then decomposed either by oxygen (ii) or by nitrogen peroxide (iii). These changes may be represented by the equations (i) $\text{SO}_2 + \text{NO}_2 + \text{H}_2\text{O} = \text{SO}_5\text{NH}_2$, (ii) $2\text{SO}_5\text{NH}_2 + \text{O} = \text{H}_2\text{O} + 2\text{SO}_5\text{NH}$, (iii) $2\text{SO}_5\text{NH}_2 + \text{NO}_2 = 2\text{SO}_5\text{NH} + \text{NO} + \text{H}_2\text{O}$. The nitrosyl-sulphuric acid formed by either of the two latter equations is then decomposed according to the equations (iv) $2\text{SO}_5\text{NH} + \text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 + \text{NO} + \text{NO}_2$, (v) $2\text{SO}_5\text{NH} + \text{SO}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{SO}_5\text{NH}_2$, the latter compound then breaking up as follows: $\text{SO}_5\text{NH}_2 = \text{NO} + \text{H}_2\text{SO}_4$, or as in (ii) or (iii). Finally, the nitric oxide is converted into the peroxide $2\text{NO} + \text{O}_2 = \text{N}_2\text{O}_4$.

P. H.

Existence of Phosphorus Sulphides: Mixtures of Phosphorus and Phosphorus Sesquisulphide. R. BOULOUGH (*Compt. rend.*, 1906, 142, 1045—1047. Compare Abstr., 1902, ii, 560; 1904, ii, 253; Giran, 1905, ii, 226).—The author finds that for a

mixture containing 33·5 per cent. of sulphur there is not a eutectic point at -40° as Giran states (*loc. cit.*). A mixture of this composition solidifies gradually, starting at $+35^{\circ}$. The eutectic point of the mixtures studied by Giran lies at about -7° , and the lower point observed by this author is probably due to the fact that these mixtures exhibit in a high degree the property of remaining in false equilibrium so that solidification is only produced by energetic cooling. The crystals so separated are isomorphous with phosphorus (compare Abstr., 1902, ii, 560).

The curve of solidification of crystals rich in P_4S_3 consists of two portions at different inclinations, and it is the intersection of the second portion with the curve of solidification of crystals rich in phosphorus which determines the eutectic point.

The point of intersection of the two portions of the curve of solidification of crystals rich in P_4S_3 occurs where the concentration of sulphur is 36 per cent. and the temperature 44° (that is, the melting point of the phosphorus), and ought to be regarded as a transition point. The most probable explanation is that above 44° phosphorus sulphide, P_4S_3 , is deposited, and below that temperature a mixture of phosphorus and phosphorus sesquisulphide. T. A. H.

Preparation of Boron Carbide in the Electric Furnace. SAMUEL A. TUCKER and H. J. W. BLISS (*J. Amer. Chem. Soc.*, 1906, 28, 605—608).—A method is described for preparing boron carbide, B_6C , by heating a mixture of boron trioxide and petroleum coke in an electric arc furnace. The furnace consists of a graphite crucible which acts as one electrode and a graphite rod suspended through the opening of the crucible, which forms the other electrode. A difficulty arises owing to the volatility of boron trioxide, but this may be obviated to some extent by placing the petroleum coke in a layer at the bottom of the furnace and adding the powdered boron trioxide through a perforation in the vertical graphite electrode.

The boron carbide described by Mühlhäuser (Abstr., 1893, ii, 570), to which he assigned the formula BC, was probably a mixture of the carbide B_6C with graphite. E. G.

Variations of State exhibited by Amorphous Carbon under the Influence of Temperature and the Action of Oscillations of Temperature. O. MANVILLE (*Compt. rend.*, 1906, 142, 1190—1193).—The temperature of formation of carbon dioxide and carbon monoxide by the direct action of oxygen on carbon depends on the nature of the carbon, its physical and chemical state, the velocity of the current of oxygen, and on the time (compare Moissan, Abstr., 1903, ii, 141). In the present paper, the author shows that when the carbon has been heated in a vacuum and cooled slowly, and the operation repeated many times, the temperatures at which it unites with oxygen to form the oxides are higher than the corresponding initial values. The experiments were conducted on powdered wood charcoal containing 89 per cent. of carbon and free from occluded gases; when this was placed in a current of oxygen, moving at the rate of one litre per hour, the temperatures of formation of carbon

dioxide and monoxide were 85° and 140° respectively; after the carbon had been heated twenty times in a vacuum from 15° to 350° and cooled slowly, the corresponding temperatures were 240° and 300° . The carbon was then heated in a vacuum to 450° and allowed to cool slowly; the temperatures of formation of carbon dioxide and monoxide were lowered to 97° and 220° respectively. Finally, the operation of heating the carbon from 15° to 350° and cooling slowly was repeated twenty times, with the result that the temperatures of formation of the higher and lower oxide rose to 245° and 307° respectively.

M. A. W.

Emission of Carbon in Certain Flames. ALESSANDRO AMERIO (*Atti Accad. Sci. Torino*, 1905—1906, 41, 328—338).—The author shows that the carbon of the flame of illuminating gas is not black, nor is it even grey for the whole length of the spectrum, but only for wave-lengths equal to or less than 1.5μ ; for greater wave-lengths, it has a relatively slight absorptive power. Nevertheless, the flame of acetylene emits carbon sensibly as a black substance. The temperature of emission of the particles of carbon in these flames, and probably also in others, such as those of petroleum, oil, &c., can be calculated on the basis of Wien's laws of displacement as if the carbon were a black substance.

T. H. P.

Explosions of Coal-gas and Air. BERTRAM HOPKINSON (*Proc. Roy. Soc.*, 1906, A, 77, 387—413).—Mixtures of coal-gas and air contained in a dumpy cylindrical vessel were fired by means of an electric spark at a point near the centre of the vessel, and the variations of temperature and pressure immediately succeeding the explosion recorded by a photographic method. The temperature measurements were made by rapidly-acting platinum thermometers placed in different parts of the vessel, the measurements of pressure by the effect on a steel piston pressing against a spring.

In mixtures rich in coal-gas containing one volume of the latter to nine of air, the maximum pressure is 78—82 lbs. above atmospheric, and is attained about one-quarter second after firing. The rate of propagation of the flame is about 150 cm. per second, and the maximum pressure is reached in less than $1/30$ second after the flame completely fills the vessel; by this time it is considered that chemical combination is practically complete. In the centre of the vessel, the gases combine approximately at atmospheric pressure, and the temperature rises to about 1225° within $1/20$ second; by subsequent adiabatic compression it rises above the melting point of platinum, probably to 1900° . Near the wall of the vessel, the gas is compressed to about five atmospheres before ignition, and the maximum temperature, in this case varying from 1100° — 1300° , is reached within $1/30$ second of the attainment of maximum pressure; in this region there is very little adiabatic compression. It is calculated that the capacity for heat of the products of explosion is about 1.3 times that of air at 1200° : a matter of great importance in the working of heat-engines. The explosion of a weaker mixture, containing 1 of gas to 12 of air, differs markedly from that of the mixture just described owing

to the fact that the rate of propagation of flame in the former mixture is so much slower, so that convection currents play an important part in the phenomenon. In this case also, the complete inflammation of the gas is nearly simultaneous with the attainment of maximum pressure, which is about 50 lbs. above atmospheric, and is reached about 2.5 seconds after the passage of the spark. G. S.

Explosive Mixtures of Coal-gas and Air. F. HÄUSER (*Chem. Centr.*, 1906, i, 311; from *J. Gasbel.*, 48, 1046—1047).—Experiments on explosive mixtures of coal-gas and air have been made in order to determine the specific heats of the chimney gases ("Rauchgase"). The apparatus consisted of a tube of about 300 c.c. capacity fitted with gas, compressed air, and vacuum connections and pressure indicator.

The abstract is taken from a review by F. HABER, who criticises the corrections which the author has made, and considers the author's conclusion, that Mallard and Le Chatelier's results are too small and that the specific heats increase as the pressure decreases, unproved.

E. W. W.

Bunsen Flame. W. ALLNER (*Chem. Centr.*, 1906, i, 309—311; from *J. Gasbel.*, 48, 1035—1040).—In the following experiments on the bunsen flame, the inner cone was completely separated from the outer in order that the gases might be sampled with greater accuracy. Haber and Richardt's conclusions (*Abstr.*, 1904, ii, 166) have been confirmed. In the relatively cold flames formed by burning mixtures of carbon dioxide and hydrogen, or of carbon monoxide and hydrogen, a state of equilibrium, however, is not attained. In the flames of mixtures of methane and hydrogen, methane, hydrogen, and carbon dioxide, benzene and hydrogen, and benzene, hydrogen, and carbon dioxide, the equilibrium $k = ([\text{H}_2\text{O}][\text{CO}])/([\text{CO}_2][\text{H}_2])$, corresponding with the temperature, is established; this also holds for the pure benzene flame, of which the temperature is about 2000°, the equilibrium being so quickly attained in this case that it extends into the cooler region.

The effect of temperature on the equilibrium is discussed in the original paper, and the values of the constant in the equation $\log K = -1/0.4343.R \int q/T^2.dt + \text{constant}$ are calculated from the different values of K and the effect of temperature on the specific heats of the gases. For the interval 1100—1600°, which is especially considered, the errors of calculation are small. The temperature of the flame can be calculated from the composition of the gaseous mixture withdrawn from the flame when the variation of the velocity constant with temperature is known ("chemical temperature"). The temperature may also be determined by means of thermoelements of varying thickness ("thermoelectric temperature"), or from the calorific values and specific heats of the gases ("calorimetric temperature"). The temperature of the coal gas flame calculated by the first two methods is about 1350°, and that of a mixture of coal gas and carbon dioxide, 1250°. In burning mixtures of carbon dioxide and hydrogen and

carbon dioxide, hydrogen, and oxygen, the hydrogen is unable to reduce the carbon dioxide at about 1000° , hence the value of the constant is found to be far less than that calculated by the calorimetric method. The presence of an accelerator in the combustion zone of flames of coal gas or of mixtures of coal gas and carbon dioxide causes a state of equilibrium to be more nearly attained. The calculated equilibrium constant and the "chemical" temperature of the carbon monoxide and hydrogen flame are both too high, but the "calorimetric" and "thermoelectric" temperatures are practically identical, hence equilibrium is not established at 1100° . Whilst in this case the temperature of the lower flame is about 1000° , and that of the upper about 1500° , in the methane-hydrogen flame the points of the inner and the outer flames have temperatures of about 1450° and about 1100° respectively. The chemical and thermoelectric temperatures agree, and when the flame is cooled by the addition of carbon dioxide the agreement still holds. The lower flame of the mixture of benzene and hydrogen is intensely green and has a temperature of about 1470° , whilst that of the dull blue upper flame is only 1270° . The lower flame is in equilibrium, and this is also the case when the flame is cooled by carbon dioxide. The internal cone of the benzene air flame is intensely green; unless the gases are thoroughly mixed, the two portions of the flame cannot be separated. It was found impossible to obtain a value for K greater than 4, although the temperature corresponding with $K=3.75$ is about 1500° , and the calorimetric temperature calculated from the composition of the gas withdrawn from the space between the flames corresponds with $K>5$. When the gas is withdrawn from the inner flame by means of a well-cooled tube, the calculated value of K is 5.8, which corresponds with a temperature of about 2200° . The composition of the gases from the inner cone must therefore remain constant on cooling if the temperature is below 1550° , whilst at higher temperatures the equilibrium changes on cooling until a temperature of about 1500° is reached. The time required for the temperature of the gases of the inner cones of the various flames to cool to about 1000° has been calculated to be 0.1 to 0.6 second.

The results are arranged in tables in the original paper and examples of some of the calculations are given in an appendix.

E. W. W.

Constitution of Carbon Suboxide. ARTHUR MICHAEL (*Ber.*, 1906, 39, 1915—1916. Compare Diels and Wolf, this vol., ii, 227).—The author considers that carbon suboxide is the lactone of β -hydroxy-

propionic acid, $\text{C} \begin{array}{c} \diagup \text{C} \\ \diagdown \text{CO} \end{array} \text{O}$.

G. Y.

The Gases of Thermal Springs. Determination of the Rare Gases; General Presence of Argon and Helium. CHARLES MOUREU (*Compt. rend.*, 1906, 142, 1155—1158. Compare Abstr., 1905, ii, 5; Bouchard and Troost, Abstr., 1896, ii, 298; Rayleigh, Abstr., 1897, ii, 316; Ramsay, Abstr., 1898, ii, 382; Moissan, Abstr., 1903, ii, 209; Nasini, Abstr., 1904, ii, 399; Curie and Laborde, *ibid.*, ii, 461).—The original contains the percentage composition by volume of

the gaseous constituents of the waters of forty-three thermal springs; the amount of rare gases present varies directly with the amount of nitrogen and inversely with the amount of carbon dioxide, being usually 1 to 1.5 per cent. that of the nitrogen, although in the waters of Maizières it is as high as 6.35 per cent. A spectroscopic examination of the rare gases revealed the presence of argon in forty-three cases and of helium in thirty-nine.

M. A. W.

Isomorphism of Potassium and Sodium Compounds. NICOLAI S. KURNAKOFF and S. SCHEMITSCHUSCHNY (*Chem. Centr.*, 1906, i, 526—528; from *Iswiestja Petersburg Polytechn. Inst.*, 1905, 4, 227—244).—In opposition to the results obtained by Le Chatelier (*Abstr.*, 1894, ii, 179) and Ruff and Plato (*Abstr.*, 1903, ii, 588), the author finds that the solidifying points of slowly cooling mixtures of the fused chlorides, bromides, iodides, or fluorides of potassium and sodium fall on a continuous curve. From the authors' observations it appears to be a perfectly general property of sodium and potassium salts to form isomorphous mixtures on crystallising from a state of fusion.

P. H.

Ultramicroscopic Examination of the Colours of Rock Salt. H. SIEDENTOPF (*Chem. Centr.*, 1906, i, 388—389; from *Physikal. Zeit.*, 6, 855—866. Compare *Ann. Physik*, 1903, [iv], 10, 1).—Natural rock salt is usually blue; the colour, which is due to ionisation, may be produced artificially by adding alkali metal or removing chlorine from the salt. In the former method, perfectly clear pieces of rock salt contained in closed tubes in an atmosphere of hydrogen are exposed to the vapour of potassium at 590° or of sodium at 680°. At temperatures near the boiling points of the metals, the salt becomes rapidly yellow, brown, green, or blue. When heated in a flame the metal is volatilised and the colour changes from blue to violet-red and pale yellow and finally disappears. All the natural and artificial colours may perhaps be due to the same cause. The natural coloration has possibly been produced by the action of strong radioactive emanations during the separation of the salt or afterwards; no trace of such emanations, however, has been found to remain in the salt. Since the colour is strongly affected by moisture, it was probably originally of a much darker shade. Ultramicroscopic examination has shown that the colour is probably caused in all cases by the metallic sodium or potassium which is contained in the fissures of the crystals. Pieces of salt which before treatment were optically transparent showed the cone of light after being coloured. Although the particles of metal are not larger than 0.4μ , they appear to have a distinct metallic lustre; the colour is not dependent on their size. Since the metal is only found in the fissures and holes of the crystals, its distribution is irregular. A thin or "molecular" coating of chloride may possibly protect the metal from the action of reagents such as chlorine. The pale yellow crystals of rock salt appear to be optically transparent, but become blue and optically turbid when gently heated owing to the fusion together of the smaller particles; when more strongly heated the fused drops again disintegrate. The blue crystals of salt appear

to be rusty brown under the ultra-microscope. The spectrum does not show, however, a sharp absorption of the *D* line; the region of absorption is broadened towards both ends of the spectrum. The optical behaviour of the particles is very dissimilar to that of optically homogeneous spheres; the particles are of an acicular or flat form according to the shape of the crystal. Wood has observed similar colours and changes of colour on the surface of pure metallic sodium which had been prepared in a vacuum. The difference between the refractive index of salt and natural rock salt is too great to be consistent with the theory of the presence of subchlorides. Since sodium and potassium have similar effects, the presence of metallic particles is probably the cause of the coloration. Colloidal blue and bluish-violet solutions of potassium and sodium have, however, been prepared. Since sodium chloride has the power of strongly absorbing Becquerel rays, the natural coloration may have been caused by ionisation or the gradual cumulative action of faint radiation. E. W. W.

Natrium Arsenicum. CARL WULFF (*Chem. Centr.*, 1906, i, 387—388; from *Apoth.-Zeit.*, 20, 1025—1029. Compare *Apoth.-Zeit.*, 19, 1010).—The preparation of disodium hydrogen arsenate, $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, is described. When the temperature of the solution is below 8° , the arsenate crystallises with $12\text{H}_2\text{O}$, but at temperatures above 8° the heptahydrate separates; the latter is best obtained by crystallising from solutions at 15 — 20° . At the ordinary temperature and under normal atmospheric conditions, the heptahydrate is completely stable; it melts at 57° , begins to lose its water of crystallisation at 30° , and is completely dehydrated when gently heated. It is very readily soluble in boiling water and dissolves in 1.64 parts of water at 15° and in about 9000 of 90 per cent. alcohol. At temperatures above 170° , the pyroarsenate is formed from the arsenate, the change taking place with rapidity at 180° . The anhydrous arsenate is prepared by heating the heptahydrate at 40 — 45° , and finally for a short time at 120° . E. W. W.

Direct Oxidation of Cæsium; some Properties of Cæsium Peroxide. ÉTIENNE RENGADÉ (*Compt. rend.*, 1906, 142, 1149—1151).—The author has examined the action of pure dry oxygen on cæsium and finds that at the ordinary temperature the cæsium is oxidised with incandescence (Graefe and Eckart, *Abstr.*, 1900, ii, 490); at -40° the oxidation proceeds rapidly but without incandescence, whilst at -80° the reaction is more gradual. When the cæsium is placed in an aluminium boat and heated in a tube containing pure dry oxygen, cæsium peroxide, Cs_2O_4 , is obtained (*Abstr.*, 1905, ii, 521), which, however, dissociates so readily that in order to obtain it pure the cæsium must be heated at 300 — 350° for some time in oxygen under atmospheric pressure and then allowed to cool slowly in contact with the gas. Cæsium peroxide has a golden-yellow colour which deepens on heating; it has a sp. gr. 3.77 at 19° and melts at 515° ; it is decomposed by water, forming cæsium hydroxide, oxygen, and hydrogen peroxide; it is reduced by dry hydrogen at 300° and reacts with

dry carbon dioxide on gently warming, forming caesium carbonate and ozone.
M. A. W.

Rubidium, Caesium, and Lithium. ROBERT DE FORCRAND (*Compt. rend.*, 1906, 142, 1252—1255).—Commercial rubidium hydroxide is the hydrate $\text{RbOH}\cdot\text{H}_2\text{O}$; it melts at 145° and loses $\frac{1}{2}\text{H}_2\text{O}$ when heated at 315° in a silver crucible, and is completely dehydrated at 350° , whilst at 400° it forms the peroxide and attacks the crucible. The heat of solution of the hydrate $\text{RbOH}\cdot\text{H}_2\text{O}$ is 3.702 Cal. at 15° , that of the pure hydroxide, RbOH , is 14.264 Cal. at 15° , whilst the intermediate compound, $\text{RbOH}\cdot 0.613\text{H}_2\text{O}$, has 7.658 Cal. at 15° . Commercial caesium hydroxide, $\text{CsOH}\cdot\text{H}_2\text{O}$, melts at 180° , begins to lose water at 400° , and is completely dehydrated after prolonged heating at 400 — 500° in a silver crucible, at which temperature the crucible is slightly attacked and caesium peroxide (Cs_2O_3 or Cs_2O_4) is formed (compare Rengade, preceding abstract). In order to obtain the pure hydroxide, the commercial hydrate must be heated in a current of dry hydrogen at 500° . The heat of solution of caesium hydroxide is 16.423 Cal. at 15° , that of the hydrate $\text{CsOH}\cdot\text{H}_2\text{O}$ being 4.317 at 15° (compare Beketoff, *Abstr.*, 1892, 274). The hydrate $\text{LiOH}\cdot\text{H}_2\text{O}$, obtained in beautiful crystals from aqueous solutions of the hydroxide, loses water when heated and forms the hydroxide, LiOH , which melts at 445° and has a heat of solution 4.477 Cal. at 24° , that of the hydrate being 0.720 Cal. at 18° .
M. A. W.

Rubidium Chromates. FRANS A. H. SCHREINEMAKERS and A. FILIPPO (*Chem. Centr.*, 1906, i, 1321—1322; from *Chem. Weekblad*, 3, 157—165. Compare this vol., ii, 287).—A saturated solution of rubidium chromate, Rb_2CrO_4 , contains 36.65 per cent. of the salt at -7.0° , 38.27 at 0° , 40.225 at 10.3° , 42.422 at 20° , 44.114 at 30° , 46.13 at 40° , 47.44 at 50° , and 48.90 at 60.4° , and solutions containing 0.949, 7.215, 9.872, 15.576, 20.027, 24.283, 30.153, 34.341, and 36.65 per cent. of chromate freeze respectively at -0.60° , -1.10° , -1.57° , -2.40° , -3.25° , -4.14° , -5.55° , -6.71° , and about -7° . The eutectic point is about -7° . As the percentage of chromic acid in the solution is increased, the compounds which separate successively in the solid state are rubidium hydroxide, chromate, dichromate, trichromate, tetrachromate, and chromic acid.

The solubility of the chromates of lithium, sodium, potassium, rubidium, and ammonium at 30° is given in percentages in the following table:

	Li.	Na.	K.	Rb.	NH ₄ .
Oxide	7.09	42.0	47.0	60.56	—
Semichromate	—	41.3	—	—	—
Chromate	49.98	46.63	39.36	44.14	28.80
Dichromate	56.6	66.4	15.34	9.47	32.05
Trichromate.....	—	about 80	decomposes	decomposes	decomposes
Tetrachromate	—	„ 76	„	„	„

All the chromates of lithium and sodium crystallise with water, but the chromates of potassium, rubidium, and ammonium are anhydrous.

E. W. W.

Lecture Experiments with Electrolytically-prepared Calcium. O. OHMANN (*Chem. Centr.*, 1906, i, 1395—1396; from *Zeit. phys.-chem. Unterr.*, 19, 83—89).—Lecture experiments showing the burning of calcium in air, in oxygen, and in the oxygen coal gas blow-pipe; the decomposition of water and water vapour, the formation of calcium hydride by passing hydrogen over the metal at a moderate heat, and the combination of calcium with chlorine, bromine, iodine, sulphur, selenium, and phosphorus are described in the original paper. The product formed by the combination of phosphorus and calcium has a sp. gr. 4.3, which is considerably greater than that of either constituent; when decomposed by water, it forms spontaneously inflammable hydrogen phosphide. The action of red phosphorus on calcium is more violent than that of yellow phosphorus, but is probably affected by the presence of water; the hydrogen phosphide obtained by the action of water on the product is in the former case only slightly spontaneously inflammable. A violent action occurs when calcium is treated with hydrochloric, sulphuric, or nitric acid, and the action of phosphoric acid is also somewhat vigorous. When ignited in an atmosphere of carbon dioxide by means of a mixture of iron and potassium chlorate, the metal burns almost as well as in air, and carbon is formed. The metal emits a shower of sparks when struck with a hammer.

E. W. W.

Bologna Phosphorus (Phosphorescent Sulphides). II. LUDWIG VANINO (*J. pr. Chem.*, 1906, [ii], 73, 446—448. Compare Vanino and Gans, *Abstr.*, 1905, ii, 248).—A radioactive lead preparation blackens a photographic plate wrapped in black paper to about the same extent when laid directly on the paper and when enclosed in a small celluloid capsule, celluloid absorbing the β - and γ -rays to only a very small extent. On the other hand, calcium and zinc sulphides, which blacken a photographic plate when laid directly on the black paper in which the plate is wrapped, have no action when enclosed in a celluloid capsule. The sulphides, therefore, do not emit Becquerel rays.

The temperature at which phosphorescent sulphides are formed is lowered by the addition of fluorspar to the mixture. As ordinary fluorspar containing iron has the same influence on the temperature of the reaction as has pure calcium fluoride, the presence of iron in small quantities cannot be detrimental. The addition of alumina or soluble aluminium salts, or the substitution of gold salts for bismuth salts, or of paraformaldehyde for starch, has no marked influence on the formation of phosphorescent sulphides. A sulphide having a varying green phosphorescence is obtained by the substitution of copper sulphate for bismuth nitrate.

A phosphorescent sulphide has been formed from a mixture containing no free sulphur; the phosphorescence in this case must be caused by traces of sulphur formed by the reduction of a part of the alkali sulphate.

Phosphorescent calcium sulphide may be mixed with indifferent substances, such as alumina or barium sulphate, without marked diminution in the intensity of the phosphorescence. Calcium sulphide suspended in water lost its phosphorescence in four months, whereas

the phosphorescence of suspensions of calcium sulphide in ether, acetone, and ethyl and amyl alcohols remained almost undiminished.

G. Y.

Plaster of Paris ALBERT MOYE (*Chem. Zeit.*, 1906, 30, 544—545).—Finely-powdered alabaster was heated in quantities of 10 grams at a time to various temperatures, and the resulting substances were allowed to cool over sulphuric acid. By determining both the sp. gr. and the amount of water of crystallisation of the several products, it was found that as the latter quantity diminished the sp. gr. rose from 2.32 to 2.75, which is the value given by van't Hoff for the half hydrate, $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$. As the amount of water was still further diminished, the sp. gr. steadily fell to 2.44, corresponding with 0.5 per cent. of water, but rose suddenly to 2.86 on complete dehydration. The substance having sp. gr. 2.44 appeared from its behaviour on exposure to moist air to be the so-called "soluble anhydrite." P. H.

Pozzuolana and its Technical Value. GIOVANNI GIORGIS and GINO GALLO (*Gazzetta*, 1906, 36, i, 137—158).—The authors give the following results of analysis of four samples of volcanic sand deposited from Vesuvius in the eruptions of: (1) 1878; (2) May, 1900; (3) November, 1900; (4) 1620:

	1.	2.	3.	4.
SiO_2	48.45	47.94	47.40	48.00
P_2O_5	0.60	0.56	0.66	—
Fe_2O_3	3.49	9.69	3.76	5.09
FeO	3.35	3.35	3.65	2.03
Al_2O_3	17.81	21.31	21.31	17.53
CaO	12.09	8.89	9.71	11.19
MgO	3.02	1.65	1.73	3.60
K_2O	5.01	5.12	5.02	8.47
Na_2O	5.46	7.33	6.38	2.56
H_2O retained at 110°	0.60	0.06	0.20	1.54
„ lost at 110°	0.41	0.17	0.13	0.36

All these samples have a less astringent taste than the pozzuolana of S. Paolo and, when mixed with lime, require hardly one-third the amount of water necessary for true pozzuolana to form a normal paste. On immersing samples (1), (2), and (3) in water and passing a current of carbon dioxide through the mixture for two months, the proportions of Na_2O present were changed to 3.95, 4.33, and 3.93 respectively, the remaining constituents being but little altered in amount. The analysis of sample (4) indicates that a similar action has occurred also with it.

The authors have determined the electrical conductivity of pozzuolana and mortars made from it with lime. The results show that adulteration of pozzuolana with inert materials may be detected in this way.

T. H. P.

Transformation of Glucinum Hydroxide into a Form Sparingly Soluble or Insoluble in Alkalis or Acids. GABRIEL VAN OORDT (D.R.-P. 165488).—Glucinum hydroxide becomes converted

into a very sparingly soluble form when heated for some time, either alone or in contact with water, steam, or a solution of some indifferent compound such as ammonia or an alkali carbonate. This change also occurs when the hydroxide is heated with aqueous alkali hydroxides so diluted that the hydroxide remains undissolved throughout the experiment. The product is also very insoluble in acids, and hence successive treatments with alkali hydroxide and acid will separate iron, aluminium, and glucinum in a mixture of their hydroxides.

G. T. M.

Alloys of Zinc and Antimony. S. SCHEMTSCHUSCHNY (*Chem. Centr.*, 1906, i, 536; from *Iswiestja Petersburg Polytechn. Inst.*, 1905, 4, 191—208. Compare Mönkemeyer, *Abstr.*, 1905, ii, 171).—Although Mönkemeyer states that the alloy ZnSb melts sharply at 561° , the present author finds that this substance decomposes at 537° into $\text{Zn}_3\text{Sb}_2 + \text{Sb}$, and does not crystallise spontaneously from the fused mass containing 53·67 to 100 atom. per cent. of antimony, but breaks up into the metastable system, $\text{Zn}_3\text{Sb}_2 + \text{Sb}$, which, on further cooling, gives the stable system $\text{ZnSb} + \text{Sb}$, a change which is accompanied with the development of a considerable amount of heat.

P. H.

Phosphorescence of Zinc Sulphide. WILLEM P. JORISSEN and WILHELM E. RINGER (*Chem. Centr.*, 1906, i, 644; from *Pub. Congrès Chim. Liège*, 1905. Compare *Abstr.*, 1904, ii, 817).—The pure sulphides of calcium, barium, or zinc do not phosphoresce except in the presence of traces of foreign matter such as bismuth salts. In the case of zinc sulphide, it is found that whereas magnesium chloride or sulphate have no action, bismuth, cadmium, or manganese salts and the chlorides of sodium or potassium produce a marked effect. The phosphorescence caused by the two latter substances is increased by the addition of manganese salts, is diminished by copper salts, and is entirely suppressed by platinum and silver salts.

P. H.

Preparation of Zinc and Magnesium Perborates. DEUTSCHE GOLD- & SILBER-SCHNEIDE-ANSTALT VORM. ROESSLER (D.R.-P. 165278 and 165279).—*Zinc perborate* may be prepared by any of the following processes: (1) a solution of boric acid and a zinc salt such as the sulphate is cooled and treated with sodium peroxide; (2) finely-divided sodium perborate and zinc chloride or sulphate are suspended in water, when metathesis occurs; (3) an aqueous suspension of sodium perborate is treated successively with a mineral acid, a solution of a zinc salt, and moderately concentrated aqueous sodium hydroxide; (4) moist hydrated zinc peroxide is triturated with boric acid, when a thin paste of zinc perborate is obtained. The first of these processes gives the best result. The perborate is an amorphous, flocculent substance containing 9·5 per cent. of active oxygen, an amount which approximates to the theoretical value.

Magnesium perborate, which can also be obtained by similar methods, is a very stable, white, amorphous powder, which evolves 11·9 per cent. of active oxygen, this being practically the theoretical amount. Digestion with water decomposes this substance into a soluble mag-

nesium hydrogen perborate and an insoluble basic magnesium perborate.
G. T. M.

Electrolytic Preparation of Copper Sulphate. GUSTAV KROUPA, LUCKOW, and ÉMILE CAMPAGNE (*Chem. Centr.*, 1906, i, 439—440; from *Oesterr. Zeit. Berg.-Hütt.*, 53, 611—613).—Cuprous and cupric oxides are prepared by electrolysing a solution of an alkali salt between copper electrodes. Sodium sulphate or chloride may be used. In the former case, copper sulphate is formed by the solution of the anode, whilst at the cathode hydrogen is liberated and sodium hydroxide formed. By the action of the alkali hydroxide on the copper sulphate, blue copper hydroxide is precipitated. An *E.M.F.* of 1·5—2 volts is required and a current density of 1 ampere per sq. metre. The theoretical quantity of copper is dissolved at the beginning of the experiment, but the *E.M.F.* soon rises to 3 volts, and oxygen is evolved at the anode, whilst the blue hydroxide of copper changes to brown or black and the liquid becomes alkaline. The occurrence of secondary reactions may be prevented by keeping the electrolyte faintly acid and in continuous circulation. When the liquid is agitated by means of a stream of carbon dioxide, cupric hydroxycarbonate, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, is formed quantitatively. In order to prevent the reduction of the oxide or carbonate by the hydrogen, the cathode is enveloped in a cotton cloth or thin felt. Copper sulphate or other salts of copper may be readily prepared from the oxide or hydroxy-carbonate; the latter forms a very fine green powder which is readily and completely soluble in dilute acids or ammonia. A sample of the hydroxycarbonate was found to contain 54·97 per cent. of copper, 19·50 of carbon dioxide, 25·23 of oxygen and water, and 0·30 of insoluble matter.
E. W. W.

Researches on the Rare Earths. II. GEORGES URBAIN (*J. Chim. Phys.*, 1906, 4, 105—139).—A continuation of the previous paper (this vol., ii, 359), which is entirely an epitome of work published by the author during the last few years. The present part deals chiefly with the various points of resemblance and isomorphism of salts of bismuth and the rare earths, and examples are given of the separation of the rare earths by means of bismuth salts as well as of the preparation of pure salts; for example, of europium and samarium (compare Abstr., 1904, ii, 37, 340, 486).
L. M. J.

Action of Ammonia Gas on Anhydrous Neodymium Chloride. CAMILLE MATIGNON and RENÉ TRANNOY (*Compt. rend.*, 1906, 142, 1042—1045. Compare Abstr., 1905, ii, 165).—When anhydrous neodymium chloride is exposed to the action of gaseous ammonia at a low temperature or is sealed in a tube with liquefied ammonia, it is converted into the *additive compound*, $\text{NdCl}_3 \cdot 12\text{NH}_3$. This, on being gradually heated, dissociates, giving rise to a series of less complex *additive products*, the formulæ, dissociation temperatures, and heats of formation (in each case from the preceding compound in the list) of which are as follows: $\text{NdCl}_3 \cdot \text{NH}_3$, 360°, 20·2Cal.; $\text{NdCl}_3 \cdot 2\text{NH}_3$, 255°, 16·9Cal.; $\text{NdCl}_3 \cdot 4\text{NH}_3$, 157°, 13·7Cal.;

$\text{NdCl}_3 \cdot 5\text{NH}_3$, 117° , 12.5Cal. ; $\text{NdCl}_3 \cdot 8\text{NH}_3$, 79° , 11.2Cal. ; $\text{NdCl}_3 \cdot 11\text{NH}_3$, 26° , 9.5Cal. ; $\text{NdCl}_3 \cdot 12\text{NH}_3$, -10° , 8.4Cal. The heats of formation were deduced by application of the law of constant change of entropy (Abstr., 1899, ii, 273). T. A. H.

Absolute Atomic Weight of Terbium. GUSTAV D. HINRICHS (*Compt. rend.*, 1906, 142, 1196—1197).—Taking the round numbers $\text{O} = 16$, $\text{H} = 1$, $\text{S} = 32$, and applying his method of limits (compare Abstr., 1893, ii, 163, 277, 316, 317; 1894, ii, 39, 87, 276; 1900, ii, 534, 539; 1905, ii, 517) to Urbain's analytical data for the determination of the atomic weight of terbium (this vol., ii, 361), the author obtains the value 159.07, as against the mean value 159.22 obtained by Urbain. M. A. W.

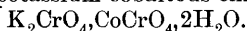
Aluminium Carbonicum. A. GAWALOWSKI (*Chem. Centr.*, 1906, i, 640; from *Pharm. Post*, 1905, 38, 756—757. Compare Abstr., 1905, ii, 713).—Aluminium carbonate varies in composition according to the method of preparation; when prepared at atmospheric pressure it contains from 8—9 per cent. of carbon dioxide and 40—45 per cent. of alumina, whilst at a pressure of 8 atmospheres a polycarbonate is obtained which dissolves to a clear solution in water; on reducing the pressure, carbon dioxide is evolved and the same carbonate is precipitated as above; the filtrate from this substance contains a soluble carbonate of aluminium, which, on warming to 25° or 30° or on keeping for some time, deposits another carbonate containing 2—3 per cent. of carbon dioxide and about 50 per cent. of alumina; this substance and the carbonate containing from 8—9 per cent. of carbon dioxide are both white, tasteless substances; they are insoluble in cold acetic acid, but dissolve readily with evolution of carbon dioxide in hot acetic acid or in mineral acids. P. H.

Variations in the Size of the Granules of Colloidal Ferric Hydroxychloride. G. MALFITANO (*Compt. rend.*, 1906, 142, 1277—1279. Compare Abstr., 1905, ii, 15, 72, 459; this vol., ii, 33).—When a colloidal solution of ferric chloride is filtered through a collodion membrane, the latter becomes stained a deep red colour, and in this modified state it is no longer impervious to the colloidal granules, but allows those portions of the colloid less rich in chlorine to pass through. If a colloidal solution of ferric chloride is diluted and then submitted to dialysis, the amount of hydrochloric acid in the filtrate increases and the number of colloidal granules diminishes with the dilution, whilst the addition of hydrochloric acid to the diluted solution causes the formation of those colloidal granules which are capable of passing through the membrane. In explanation of these facts, the author suggests that the original colloidal solution contains a mixture of granules each formed of 1, 2, 3, or 4 mols. $\text{Fe}_2(\text{OH})_6$ grouped round the H ion of an HCl molecule; the smaller granules, those containing 1 or 2 mols. $\text{Fe}_2(\text{OH})_6$, are able to percolate through the membrane, whilst the larger ones are incapable of so doing; the effect of dilution on the colloidal solution is to increase the hydrochloric acid at the expense of the chlorine of the smaller colloidal

granules, which are re-formed on the addition of hydrochloric acid to the diluted solution. M. A. W.

Action of Silicon Tetrachloride on Nickel. ÉMILE VIGOUROUX (*Compt. rend.*, 1906, 142, 1270—1271. Compare this vol., ii, 32, 287).—When nickel is subjected to the action of silicon tetrachloride at a high temperature until the mass fuses and the loss in weight amounts to 30 per cent., the product consists of the *silicide*, Ni_4Si , which has a metallic appearance, is very brittle and crystalline, and not attracted by a magnet. By the prolonged action of silicon tetrachloride on the lower silicide, it is converted into the higher silicide, Ni_2Si (compare Abstr., 1896, ii, 176). M. A. W.

Cobalt Chromates. MAX GRÖGER (*Zeit. anorg. Chem.*, 1906, 49, 195—206. Compare Abstr., 1905, ii, 393).—Aqueous solutions of cobalt chloride were mixed with solutions of potassium, sodium, and ammonium chromates of different strengths and the composition of the precipitates investigated. The only definite crystalline compound isolated was the normal potassium cobaltous chromate,



The precipitates obtained with sodium chromate form dark brown granules and consist essentially of basic cobaltous chromates together with small quantities of a higher oxide of cobalt. When sodium chromate is used in considerable excess, the precipitates contain varying quantities of this salt as well. All the precipitates obtained with potassium chromate contain considerable quantities of this salt and are to be regarded as potassium cobaltous chromates. They are, however, slowly hydrolysed even by cold water, giving up potassium chromate, until finally basic chromates of cobalt remain. From a solution of equivalent quantities of cobalt chloride and the chromate, the *compound* $\text{K}_2\text{CrO}_4, \text{CoCrO}_4, 2\text{H}_2\text{O}$ was obtained in dark brown needles. The precipitates obtained with ammonium chromate were brownish-red in colour and contained ammonium, but no crystalline double salt corresponding with the potassium compound could be obtained. By repeated treatment with water, all the ammonium chromate can be removed, and basic cobalt chromates, mixed with varying proportions of a higher oxide of cobalt, remain behind. G. S.

Behaviour of Chromium prepared by the "Aluminothermal Method" towards Hydrogen Haloids. THEODOR DÖRING (*J. pr. Chem.*, 1906, ii, 73, 393—419. Compare Abstr., 1902, ii, 660).—The experiments described in this paper were carried out with the least impure of the three preparations of chromium quoted previously (*loc. cit.*). It contains 97·95 per cent. of chromium, and is more stable towards hydrobromic, hydriodic, and hydrofluoric acids than is the most impure preparation containing 93·67 per cent. of chromium. The chromium is dissolved completely by moderately concentrated hydrofluoric acid, but small amounts remain undissolved often, even on prolonged heating with concentrated hydrobromic or hydriodic acid. The minimum concentration at which the acid acts on the chromium is, at

the ordinary temperature for hydrobromic acid, 1.40—1.60, for colourless hydriodic acid 2.20—2.40, and for hydrofluoric acid 1.32—1.50 gram-mols. per litre, or, at the boiling point of the acids, 0.22—0.28, 1.70—2.00, and 0.22—0.28 gram-mols. per litre respectively. The solutions in hydrobromic and hydrofluoric acids are at first bluish-green, and become pure green or bluish-violet only when the reaction has proceeded for some time. The solution in hydrofluoric acid is green from the commencement of the reaction. The solutions formed at the ordinary temperature contain only very small amounts of the chromous haloids.

When dissolved at higher temperatures in an atmosphere of hydrogen, chromium forms in hydrofluoric acid a green, in hydrobromic or hydriodic acid a blue, solution, becoming green or violet only after some hours. These solutions contain considerable amounts of the chromous together with the chromic haloids. The change of the chromous haloid first formed into the chromic haloid is accompanied by an evolution of hydrogen, which may be observed after the metal has been entirely dissolved. The change takes place rapidly and completely in the presence of platinum black.

The results of the quantitative study of these changes are tabulated and plotted as curves.

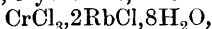
The change of the chromous into the chromic haloid commences at the same time or immediately after the formation of the chromous haloid. The amount of the chromic haloid formed increases with the concentration of the chromium in the solution. This confirms the author's view of the nature of Ostwald's periodic curve.

The concentration of the chromous haloid increases to a maximum after an interval varying with the acid, and thereafter gradually diminishes. In hydrochloric acid solution, the concentration of the chromic chloride is always greater than that of the chromous chloride, whilst the concentration of the chromous haloid may be the greater in hydrobromic or hydriodic acid solution. The velocity of the actual process of solution increases rapidly to a maximum and then diminishes.

G. Y.

Chromium Compounds. IV. Hydrated Chromium Chlorides.

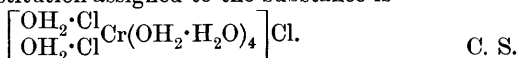
ALFRED WERNER and A. GUBSER (*Ber.*, 1906, **39**, 1823—1830. Compare Abstr., 1901, ii, 453).—Godefroy's decahydrated chromic chloride (Abstr., 1885, 352), more conveniently obtained from a solution of chromic chloride (2 : 1) cooled in a freezing mixture, separates in needle-shaped or prismatic crystals, which are stable in air at the ordinary temperature, dissolve readily in water, alcohol, or acetone, and lose 4H₂O over sulphuric acid, changing into the green hexahydrate. Only one-third of the chlorine is precipitated by silver nitrate, and the electrical conductivity also indicates the presence of only two ions in solution. Of the 10H₂O, two mols. are replaceable by rubidium chloride, forming a green, crystalline, unstable *double salt*,



in which two-fifths of the chlorine is not precipitated by silver nitrate.

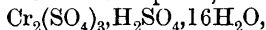
These properties show that the decahydrate is of the same type as the

green hexahydrate (*loc. cit.*); the additional $4\text{H}_2\text{O}$ are in the chromium complex, and the constitution assigned to the substance is



Violet Sulphates of Chromium. RUDOLF F. WEINLAND and REINHOLD KREBS (*Zeit. anorg. Chem.*, 1906, 49, 157—171. Compare this vol., ii, 233; Higley, *Abstr.*, 1905, ii, 565).—The violet chlorosulphate of chromium described in a former paper is decomposed by water, and from the solution a hydrated chromium sulphate with $17\text{H}_2\text{O}$ was obtained in long, tabular, violet crystals. Attempts were made to prepare the violet octahedral sulphate with $18\text{H}_2\text{O}$, described by Higley (*loc. cit.*) and others, but without success; in all cases the tabular crystals with $17\text{H}_2\text{O}$ were obtained.

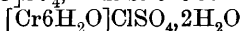
Three violet acid sulphates of chromium were obtained by the action of excess of strong sulphuric acid on aqueous solutions of chrome alum in the cold. In a vacuum over sulphuric acid, when 100 molecules of the acid are present to one of the sulphate, the tetrasulphate,



separates in columnar crystals; with 140 molecules of the acid, the pentasulphate, $\text{Cr}_2(\text{SO}_4)_3, 2\text{H}_2\text{SO}_4, 18\text{H}_2\text{O}$, is obtained in rectangular plates. By interaction of the components at -15° , a second tetrasulphate, $\text{Cr}_2(\text{SO}_4)_3, \text{H}_2\text{SO}_4, 24\text{H}_2\text{O}$, is obtained in the form of long, tabular crystals. A green tetrasulphate, isomeric with the first-mentioned salt, was obtained in fine needles from a solution previously warmed.

In a vacuum over sulphuric acid, the salt with $16\text{H}_2\text{O}$ remains unaltered, whilst that with $24\text{H}_2\text{O}$ loses 8 molecules of water and yields the former salt. The pentasulphate, on abstraction of water, becomes greyish-green in colour, but does not attain a constant weight even after two months. It is considered that the sulphuric acid residues in all these salts are ionised, and from their behaviour the formulæ $[\text{Cr}_2, 16\text{H}_2\text{O}](\text{SO}_4)_3, \text{SO}_4\text{H}_2$ and $[\text{Cr}_2, 16\text{H}_2\text{O}](\text{SO}_4)_3, \text{SO}_4\text{H}_2, 8\text{H}_2\text{O}$ are ascribed to the tetrasulphates, and that of $[\text{Cr}_2, 18\text{H}_2\text{O}](\text{SO}_4)_3, 2\text{SO}_4\text{H}_2$ to the pentasulphate.

As a result of further experiments, particularly of electrical conductivity measurements, it has been found that the formulæ ascribed to the green and violet chlorosulphates in the former paper (*loc. cit.*) are no longer tenable; it is now considered that the green salt has the formula $[\text{CrCl}5\text{H}_2\text{O}, 3\text{H}_2\text{O}]\text{SO}_4$, whilst the formula



is ascribed to the violet salt.

G. S.

Pure Ferrotungstens. ÉMILE VIGOUROUX (*Compt. rend.*, 1906, 142, 1197—1199).—By igniting a mixture of iron oxide, the lower oxide of tungsten (WO_2), and aluminium in different proportions, the author has obtained three homogeneous iron-tungsten alloys containing respectively 2.3, 6.21, and 46.25 per cent. of tungsten. These alloys are attacked by dilute hydrochloric acid, which dissolves the uncombined iron, leaving the ferrotungsten Fe_3W_2 (compare de Benneville, *Abstr.*, 1896, ii, 174)

in the form of brilliant plates, with a sp. gr. 13.89 at 0°; it is not sensibly attracted by the magnet, is readily attacked by chlorine at 350°, by oxygen or the alkali carbonates at a bright red heat, or by potassium hydrogen sulphate at a dull red heat; whilst aqua regia, sulphuric acid, fused potassium chlorate or nitrate have very little action on the compound.

The original contains a complete bibliography of the ferrotungstens.
M. A. W.

Tin Sulphides, Selenides, and Tellurides. HENRI PÉLABON (*Compt. rend.*, 1906, 142, 1147—1149).—The freezing-point curve for mixtures of tin and sulphur rises rapidly from 232°, the freezing point of tin, to 840°, the freezing point of the mixture containing 5 per cent. of sulphur, and then rises more gradually to the maximum point 880°, the freezing point of stannous sulphide; beyond this point the mixtures lose sulphur on being heated, but their melting points are lower than 880°. A mixture of tin and sulphur in the proportion required for the sesquisulphide, Sn_2S_3 , decomposes on fusion, yielding a sublimate of stannic and a residue of stannous sulphide.

The freezing-point curve for mixtures of tin and selenium closely resembles the preceding; it rises first rapidly, then more gradually, to the maximum point 860°, the melting point of stannous selenide, SnSe , then falls rapidly to 655° and 640°, the two freezing points of the mixture corresponding with the sesquiselenide, Sn_2Se_3 ; after that the curve falls very gradually to 550°, the freezing point of the mixture containing 30 atoms of selenium to one of tin, and shows no peculiarity for the mixture $\text{Sn} + \text{Se}_2$.

The freezing-point curve for mixtures of tin and tellurium rises first rapidly, then more gradually, to 780°, the freezing point of stannous telluride, which is also the maximum point, then falls rapidly to the minimum point 388°, the melting point of the eutectic mixture, which contains about 87 per cent. of tellurium, after which it rises to 452°, the melting point of tellurium. The curve presents no peculiarity for the mixtures $\text{Sn}_2 + \text{Te}_3$ or $\text{Sn} + \text{Te}_2$.
M. A. W.

Mineralogical Chemistry.

Hemihedrism of Sylvite. OTTO MÜGGE (*Centr. Min.*, 1906, 259—261).—The plagiohedral-hemihedral degree of symmetry of sylvite has hitherto been based only on the evidence afforded by etched figures. The crystals now described consist of interpenetrating cubes, twinned on an octahedral face: each cube-face is replaced by a low, four-sided pyramid placed skew-wise on the face. All the crystals observed are right-handed. They were deposited at the ordinary temperature during a period of several years from a concentrated solution of potassium chloride.

L. J. S.

Crystals of Sylvite in Blocks ejected during the Recent Eruption of Vesuvius. ANTOINE LACROIX (*Compt. rend.*, 1906, 142, 1249—1252).—Some of the pieces of rock ejected during the recent eruption of Vesuvius contain a large quantity of crystalline alkali salts, chiefly sylvite, which occurs in large, cubic crystals; the cube-faces are generally brilliant, but some of them present the well-developed, rounded faces of the hexakisoctahedra; the crystals are either transparent and colourless, or opalescent and of a bluish-white colour. In some specimens, large cubic crystals of sodium chloride (rock salt), exhibiting octahedral faces, are found associated with the sylvite; and also citron-yellow, monoclinic crystals, of a triple chloride of sodium, potassium, and manganese, possessing the following optic properties: the acute bisectrix is positive and parallel to the vertical axis, there is no pleochroism, and the double refraction is a little higher, and the refraction greater, than that of sylvite; the mineral is probably identical with the *chloromanganokalite* described by Johnston Lavis (*Nature*, 1906, May 31). M. A. W.

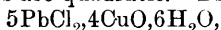
Paratacamite, a new Copper Hydroxychloride. G. F. HERBERT SMITH, with analysis by GEORGE T. PRIOR (*Min. Mag.*, 1906, 14, 170—177).—The following analysis shows the new mineral to have the same composition as the orthorhombic atacamite, $\text{Cu}_2\text{Cl}(\text{OH})_3$.

CuO.	Cu.	Cl.	H ₂ O.	Total.	Sp. gr.
56.10	14.27	15.97	14.10	100.44	3.74

Although the crystals are optically biaxial, their external symmetry is rhombohedral ($C=1.0248$); they are invariably twinned on a rhombohedron plane, and are either rhombohedral or prismatic in habit. The colour is bright green. The water of atacamite is expelled only slightly more readily than that of paratacamite. L. J. S.

Boleite and Related Minerals. GEORGES FRIEDEL (*Chem. Centr.*, 1906, i, 1566—1567; from *Bull. Soc. franç. Min.*, 29, 14—55).—Cumengeite, $4\text{PbCl}_2.4\text{CuO}.5\text{H}_2\text{O}$, crystallises in very slightly polychroic, indigo-blue, quadratic octahedra. Sp. gr. 4.67 at 18.7°.

Boleite, $9\text{PbCl}_2.8\text{CaO}.3\text{AgCl}.9\text{H}_2\text{O}$, crystallises in deep indigo-blue cubes, sometimes combined with the regular octahedron and the rhombododecahedron; thin plates appear green by transmitted light. Sp. gr. 5.05 at 18.7°. From the complicated cleavage it is inferred that the crystals are quadratic. Pseudoboleite,



resembles boleite in appearance and is always found in conjunction with it, and frequently with cumengeite; the negative uniaxial crystals have the sp. gr. 4.996 at 17°. E. W. W.

Crystalline Form of Pyrrhotite. ERICH KAISER (*Centr. Min.*, 1906, 261—265).—In a long series of papers on the magnetic characters of pyrrhotite, P. Weiss has shown that the crystals are diamagnetic in a plane parallel to the base, but paramagnetic in a direction perpendicular thereto; further, from the variations in the strength of

the magnetisation in different directions in the basal plane, he has concluded that the crystal-system is monoclinic. A discussion of Weiss's results leads the present author to the conclusion that the crystals are orthorhombic and pseudo-hexagonal, and that the pseudo-hexagonal symmetry is increased by repeated twinning, as in aragonite, &c.

L. J. S.

Mineralogy of Sardinia. Bournonite from Sarrabus. FEDERICO MILLOSEVICH (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 457—461).—The author describes specimens of bournonite found above a matrix of compact quartz in the Canale Figu vein near Sarrabus, associated with blende, argentite, native silver, pyrites, and perhaps also tetrahedrite. The crystals mostly exhibit twinning, four individuals being commonly combined to form a cruciform aggregate, although in many cases a greater number of crystals are associated. Measurements give for the axial ratios the values $[a : b : c = 0.93415 : 1 : 0.89410]$. T. H. P.

Regular Intergrowth of Rutile and Hæmatite. HEINRICH BAUMHAUER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1906, 322—327).—Determination of the crystallographic orientation of the two minerals.

L. J. S.

Aragotite from California. HENRY G. HANKS (*J. R. Microsc. Soc.*, 1905, 673—676).—Ores of mercury are frequently associated with hydrocarbons, and a yellow, resinous substance from the Almaden mercury mine in California was described by F. E. Durand in 1872 under the name aragotite. A similar substance from the Aetna mercury mine in Napa Co., California, is honey-yellow and transparent and has a white streak; the hardness is 1; the sp. gr. 1.1; melting point 125°. It is completely soluble in oil of turpentine and petroleum, but is only partially soluble in alcohol. It contains: C, 88.10; H, 9.17 per cent. These characters separate it sharply from idrialite, with which the substance was compared by Durand.

L. J. S.

Dundasite from North Wales. GEORGE T. PRIOR (*Min. Mag.*, 1906, 14, 167—169).—This mineral has previously been recorded only from Tasmania and has not been before completely analysed (Abstr., 1904, ii, 47). The following analysis of the Welsh mineral gives the formula $\text{PbO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{CO}_2 \cdot 4\text{H}_2\text{O}$ or $\text{PbH}_2(\text{CO}_3)_2 \cdot \text{Al}_2(\text{OH})_6$.

PbO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	CO ₂ .	H ₂ O (>100°).	H ₂ O (100°).	Insol.	Total.	Sp. gr.
43.20	21.39	1.61	16.45	13.60	1.41	1.80	99.46	3.25

The mineral occurs as white, spherical aggregates or tufts of minute, radiating, birefringent needles, with cerussite and allophane, in the Welsh Foxdale mine, near Trefriw in Carnarvonshire.

L. J. S.

Formation of Oceanic Salt Deposits. XLVII. JACOBUS H. VAN'T HOFF and J. D'ANS (*Sitzungsber. K. Akad. Wiss. Berlin*, 1906, 20—22, 412—419. Compare Abstr., 1905, ii, 175, 262, 319, 464, 641; 1906, ii, 236).—The limits of the polyhalite and krugite region at 83° have been established. Of the ten observations necessary for this

purpose, the following six have been determined directly: (1) and (2) the limits between glauberite and polyhalite in different regions, (3) between syngenite and polyhalite, (4) the occurrence of glauberite, polyhalite, and syngenite together in the glaserite region, (5) syngenite, polyhalite, and penta-salt together in the potassium chloride region, (6) polyhalite, penta-salt, and anhydrite together in the potassium chloride region; the remaining limits were determined by the application of Wilson's rule (Abstr., 1900, ii, 285), according to which, in certain saturated solutions, $1/3\cdot4$ molecule of magnesium chloride (in this case calcium chloride) always replaces one molecule of K_2Cl_2 at 83° . In the course of the investigation it was found that limits can in some cases be rapidly determined by vapour pressure measurements with the tensimeter.

The most noticeable difference in the polyhalite and krugite region at 25° and 83° is its great extension at the latter temperature; it is found to project some distance into the region of solutions containing calcium chloride, which is important from the mineralogical point of view.

G. S.

Chrysotile from Cyprus. JOHN W. EVANS (*Min. Mag.*, 1906, 14, 143—148).—Historical notes are given respecting the Karystian stone or amiantos of the ancients, who obtained it from Karystos, in Eubœa, and from Cyprus; and the conclusion is drawn that the material is identical with chrysotile (fibrous serpentine) rather than with asbestos (fibrous hornblende). Material from the ancient quarries on the south-east of Mount Troodos, in Cyprus, has the characters of chrysotile; analysis by G. S. Blake gave:

SiO ₂ .	Al ₂ O ₃ .	FeO.	MgO.	H ₂ O (>100°).	H ₂ O (100°).	Total.
40·54	1·09	4·87	39·02	13·47	1·13	100·12

L. J. S.

Microscopical Characters of Sarcolite. ANTON PAULY (*Centr. Min.*, 1906, 266—270).—The difficulty experienced in determining sarcolite in rock-sections led to a redetermination of the characters of this mineral. The material examined consisted of Vesuvian crystals. The axial ratio, $a:c=1:0\cdot8840$; there is a fairly distinct cleavage parallel to the prism (110). Hardness 5—6; sp. gr. 2·7. Refractive indices for sodium light, $\omega=1\cdot6404$, $\epsilon=1\cdot6566$; optically uniaxial and positive. The following analysis agrees with the usually accepted formula, $(Ca,Na_2)_3Al_2Si_3O_{12}$ or $3RO,Al_2O_3,3SiO_2$:

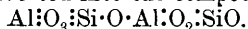
SiO ₂ .	Al ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	Total.
39·34	21·63	33·70	0·36	4·43	trace	99·46

The optical characters by which sarcolite may be distinguished from other rock-forming minerals are enumerated.

L. J. S.

Constitution of Certain Natural Silicates. H. C. McNEIL (*J. Amer. Chem. Soc.*, 1906, 28, 590—602).—Experiments have been made with the object of ascertaining the constitution of certain minerals. The minerals, both before and after ignition, were heated

with solution of sodium carbonate and also with hydrochloric acid in order to determine the amounts of silica and aluminium oxide liberated under certain conditions. In the case of talc, the results indicate that this mineral contains both an ortho- and a tri-silicate radicle and that, on ignition, the latter is transformed into a Si_2O_5 group. Kaolin is probably an orthosilicate, $\text{Al}:\text{O}_3:\text{Si}\cdot\text{O}\cdot\text{Al}(\text{OH})\cdot\text{O}\cdot\text{Si}(\text{OH})_3$, which on ignition is converted into the compound



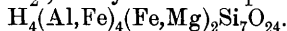
Halloysite is represented by the same formula as kaolin with 1 mol. of water of crystallisation. Pyrophyllite may be regarded as a true acid metasilicate.

When analcite is fused with barium chloride, the sodium is completely replaced by barium, but this change is accompanied by a considerable breaking down of the analcite molecule. Similar results are obtained with strontium chloride. When chabazite is fused with barium chloride or sodium chloride, substitution takes place with formation of a compound containing chlorine. Similar results are obtained with stilbite and thomsonite. From these experiments, the general formula $[(\text{AlO}_2\text{H}_2)_2\text{H}_2:\text{X}\cdot\text{Al}(\text{X}:\text{Al})\cdot\text{X}(\text{R})]_2\text{R}$ is suggested for thomsonite, stilbite, and chabazite, in which X represents chiefly the SiO_4 group in thomsonite, principally Si_3O_8 in stilbite, and nearly equal quantities of each in chabazite.

In the course of this work, it was observed that under certain conditions silica and aluminium oxide are soluble in fused barium chloride.

E. G.

Leptochlorites from Moravia. FRANZ KRETSCHMER (*Centr. Min.*, 1906, 293—311).—A description is given of the occurrence of chloritic minerals (leptochlorites) with the iron ores in connection with diabase and Schalestein at Gobitschau, near Sternberg (compare *Ann. Rep.*, 1905, 2, 281, 290). The name *moravite* is applied to a mineral occurring as finely scaly aggregates with an iron-black colour and semi-metallic lustre. Although resembling thuringite in appearance, it differs from this in chemical, optical, and other characters. Sp. gr. 2·38; hardness $3\frac{1}{2}$; analysis I corresponds with



A second analysis made on rather less pure material is given under II. Under the microscope the material is colourless (and can thus be readily distinguished from the green thuringite with which it is intimately associated); it is birefringent and optically negative.

	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	MnO .	CaO .	MgO .	P_2O_5 .	H_2O .	Total.
I.*	49·30	22·71	5·04	13·99	nil	trace	1·82	trace	4·95	99·46
II.	50·69	19·62	10·42	8·30	nil	0·84	1·46	0·93	5·02	97·28
III.	23·80	17·17	14·59	27·41	0·16	0·51	2·70	0·19	13·23	99·76
IV.	28·85	17·03	11·44	26·03	0·50	1·92	2·75	1·24	10·00	99·76
V.	24·50	18·45	11·23	31·20	0·07	0·93	2·86	0·44	9·93	99·59

* Also $\text{K}_2\text{O} + \text{Na}_2\text{O}$, 1·10; graphite, 0·55.

Analyses III—V are of thuringite from the same locality.

L. J. S.

Possible Relation between the Viscosity Curves and the Molecular Volumes of Silicates. FRANZ LOEWINSON-LESSING (*Centr. Min.*, 1906, 289—290).—The viscosity curves of silicates recently given by C. Doelter (this vol., ii, 350) are of two different types. Those for olivine, pyroxenes, and magnetite exhibit a break near the melting point, whilst those for the feldspars, and perhaps also nepheline, are continuous. In 1897, the present author pointed out that there is another distinction between these two groups of minerals: with the feldspars and leucite and nepheline, the molecular volumes are greater than the sums of the molecular volumes of the component oxides, whilst with olivine and the pyroxenes they are smaller. The greater viscosity of the feldspars is thus probably due to the opposing effect of the dilation accompanying fusion and the contraction due to dissociation.

L. J. S.

Rhodonite from Chiaves and from other Localities of the Valli di Lanzo. ALESSANDRO ROCCATI (*Atti R. Accad. Sci. Torino*, 1906, 41, 487—494).—Rhodonite found at Chiaves and having the sp. gr. 3.59 gives on analysis the numbers:

SiO ₂ .	MnO.	FeO.	CaO.	MgO.	Total.
43.18	53.25	0.67	1.33	1.02	99.45

This indicates the formula MnSiO₃, some of the manganese being replaced by iron, calcium, and magnesium. Rhodonite has also been found at Viù, Ceres, Ala, Coassolo, and Balangero.

T. H. P.

Geikielite and the Ferro-magnesian Titanates. THOMAS CROOK and BERNARD MOUAT JONES (*Min. Mag.*, 1906, 14, 160—166. Compare Abstr., 1903, ii, 84).—A new analysis of the original geikielite from Ceylon (Abstr., 1895, ii, 509) gave the results under I, proving the formula to be (Mg,Fe)TiO₃ rather than MgTiO₃. This is borne out by several other analyses (II—X) of geikielite from Ceylon. The ferric oxide shown in these analyses is in some cases primary (isomorphously replacing the geikielite molecule), whilst in others it has resulted from the alteration of ferrous oxide. With an increase in the amount of iron there is a passage to magnesian ilmenite or picroilmenite (analyses XI and XII), with a corresponding increase in sp. gr.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
TiO ₂ ...	63.77	64.78	64.41	63.94	64.03	62.49	62.25	61.60	60.87	60.02	57.64	56.08
FeO ...	6.34	5.92	5.44	10.09	12.14	10.70	11.58	7.79	6.03	5.81	16.57	24.40
Fe ₂ O ₃ ..	1.93	2.22	2.77	0.25	—	3.54	—	4.95	5.69	6.80	10.17	5.43
MgO ...	28.50	27.90	27.90	25.79	24.66	23.60	26.03	26.31	27.29	27.79	15.56	14.18
	100.54	100.82	100.52	100.07	100.83	100.33	99.86	100.65	99.88	100.42	99.94	100.09
Sp. gr.	—	3.89	3.97	4.01	4.11	4.01	3.91	3.90	3.87	3.79	4.17	4.25

The material is jet-black in colour and has a purplish-brown streak; thin splinters are translucent with a deep reddish-purple colour. The alteration products are similar to those of ordinary ilmenite, namely, rutile, leucoxene, sphene, and limonite. Cleavage surfaces are frequently coated with leucoxene, which, as shown by the

following analysis, consists mainly of amorphous titanium dioxide with some sphene :

TiO ₂ .	Fe ₂ O ₃ .	CaO.	MgO.	SiO ₂ .	H ₂ O	Total.
81·3	6·4	3·0	trace	4·2	5·6	100·5

L. J. S.

Physiological Chemistry.

Proteid Chemistry and Physiology. EMIL ABDERHALDEN (*Chem. Centr.*, 1906, i, 248—249; from *Med. Klin.*, 1905, Nos. 46 and 47. Compare Abstr., 1905, i, 496).—A discussion of work already published.
H. M. D.

Apnoea and Carbon Dioxide in the Inspired Air. S. WEIL (*Chem. Centr.*, 1906, i, 1367; from *Arch. exp. Path. Pharm.*, 54, 285—293).—The experiments were made on rabbits in which respiratory reflexes were prevented by narcotising them with chloral. Carbon dioxide in the air lessens the duration of apnoea, and above a certain limit (5·4 per cent.) powerful artificial respiration causes no apnoea at all. The cause of apnoea is not increase of oxygen, but lessening of carbon dioxide in the blood.
W. D. H.

Ammonia in the Expired Air and Blood. GUIDO PICCININI (*Chem. Centr.*, 1906, i, 1501; from *Arch. Farm. sper.*, 5, 36—54).—Expired air was collected by a tracheal tube in dogs and rabbits. It contained a small amount of ammonia; this remains constant, or may increase with rectal or intravenous administration of ammonia or its salts. It markedly increases in uræmia. Ammonia is also found in the distillate of blood, especially if a stream of air is passed through the fluid.
W. D. H.

Coagulation of Blood. PIERRE NOLF (*Bull. Acad. roy. Belg.*, 1906, 71—87. Compare Morawitz, Abstr., 1904, ii, 59).—The author shows that "fibrin-ferment" or thrombin is a combination of two substances: leucothrombin, secreted by leucocytes and possessing in a marked degree the property of coagulating blood plasma, and hepatothrombin, secreted by the liver. Hepatothrombin is identical with the antithrombin recognised by several physiologists as occurring in the plasma of peptone, and to which the incoagulable nature of this material has been attributed. Depending on the relative amounts of these two constituents present in blood plasma, three sets of conditions may occur: (1) leucothrombin in excess, when coagulation is rapid; (2) hepatothrombin in excess, when a permanent clot is formed very slowly; and (3) when the two constituents are in functional equilibrium, in which case coagulation is rapid and the clot formed is permanent.

Thrombin is rendered inactive when heated to 56° , but the constituents, leucothrombin and hepatothrombin, survive exposure to somewhat higher temperatures. The experiments from which these conclusions have been drawn and the application of these results to a number of physiological problems are discussed in the original.

T. A. H.

The Relations of the Inorganic Salts of the Blood to the Contractions of Cardiac and Skeletal Muscle. E. G. MARTIN (*Amer. J. Physiol.*, 1906, 16, 191—220).—Howell's hypothesis, which assigns to the inorganic salts of the blood a function of arousing the "inner stimulus" which produces the contraction of the heart, is not supported. The products of the tissue's own metabolic activity form more probably the source of the stimulation. Calcium ions favour the response of skeletal muscle to normal stimulation, as they do also the response of the heart to its "inner stimulus." It is suggested that the action of diffusible calcium ions in promoting oxidation may be in the nature of the activation of enzymes. The assumption that sodium ions exert their influence through mass action is supported by the fact that they are only effective when present in quantity. The view is advanced that diffusible potassium ions cause inhibition by forming inactive compounds with the zymogens and contractile substances of the tissue. The experiments were made on heart strips.

W. D. H.

The Composition of the "Residual Nitrogen" in Blood and Serous Fluids. CARL NEUBERG and H. STRAUSS (*Chem. Centr.*, 1906, i, 1558; from *Berl. Klin. Woch.*, 43, 258—260).—A comparison of the amounts of amino-acids (of which glycine was identified) in the residual nitrogen of the blood and serous exudations in various pathological conditions. The causes of variation are discussed.

W. D. H.

Catalases of Blood. LEOPOLD VAN ITALLIE (*Chem. Centr.*, 1906, i, 691—692; from *Pharm. Weekblad*, 43, 27—32. Compare this vol., ii, 238).—Catalases are widely distributed in the animal and vegetable kingdoms, and have the power of decomposing hydrogen peroxide into oxygen and water. They occur in the blood, but to varying degrees of activity in different animals; a further difference between them is seen in their resistance to an elevated temperature, some being destroyed at a lower temperature than others.

W. D. H.

Examination of Body Juices. LEOPOLD VAN ITALLIE (*Chem. Centr.*, 1906, i, 692; from *Pharm. Weekblad*, 43, 33—35).—An aqueous extract of blood shows catalase reactions which are destroyed in greater or less measure at 63° . The same holds true for certain other fluids, of which milk was specially investigated. The power of cow's milk to decompose hydrogen peroxide is destroyed at 63° , whereas it is only slightly lessened in the case of human milk.

W. D. H.

Action of Fluorescent Substances on Toxins. A. JODLBAUER and HERMANN VON TAPPEINER (*Chem. Centr.*, 1906, i, 577—578 ; from *Arch. Klin. Med.*, 85, 399—415).—Many photo-dynamic substances lessen the agglutinating action of ricin and the hæmolytic action of crotin in the light. They lessen the toxic properties of diphtheria and tetanus toxins.
W. D. H.

Further Investigations whether Fluorescent Substances Act in the Dark. A. JODLBAUER (*Chem. Centr.*, 1906, i, 576—577 ; from *Arch. Klin. Med.*, 85, 395—398).—Straub (*Arch. exp. Path. Pharm.*, 1904, 51, 583) states that eosin and quinine liberate iodine from potassium iodide in the dark. The present experiments do not confirm this statement. These substances also have no action in the dark on enzymes or on agglutinin reactions.
W. D. H.

Complementoids. HANS SACHS (*Chem. Centr.*, 1906, i, 377—378 ; from *Centr. Bakt. Par.*, i, 40, 125—129).—The existence of complementoids, originally described by the author with Ehrlich, and denied by Gay, is defended.
W. D. H.

Peptic Digestion. PAUL MEY (*Zeit. physiol. Chem.*, 1906, 48, 81—84).—By the use of tannin, the proteoses formed in gastric digestion can be precipitated almost entirely. A peptone (in Kuhne's sense) remains in the filtrate.
W. D. H.

The Proteolytic Ferments of the Pyloric and Duodenal Juices. EMIL ABDERHALDEN and PETER RONA (*Zeit. physiol. Chem.*, 1906, 47, 359—365).—Ferments at present can only be identified by their actions. Their action on certain polypeptides is a distinguishing mark. For instance, glycyl-*L*-tyrosine is readily decomposed into its constituents by trypsin, but not by pepsin-hydrochloric acid. Glycyl-glycine is similarly split up by liver extract, but not by pancreatic juice. In the present research, pure duodenal and pyloric juices were obtained from fistulæ in dogs, the operations being performed by Pawloff. These are clear watery fluids, the former containing mucin. They do not decompose glycyl-*L*-tyrosine in neutral, alkaline, or acid media ; they contain proteolytic enzymes of the pepsin, not the trypsin type.
W. D. H.

The Enzymes contained in Food and their Rôle in Digestion. ARTHUR SCHEUNERT and WALTHER GRIMMER (*Zeit. physiol. Chem.*, 1906, 48, 27—48).—In a large number of vegetable foods (hay, grains, rice, potatoes, &c.), a ferment is present which is destroyed by boiling, but which at body-temperature converts starch into dextrins and sugar. Some of these differ from ptyalin by acting readily in an acid medium, and therefore in the stomach. An enzyme capable of producing lactic acid is also present. In oats, maize, lupins, vetches, horse beans, and buck-wheat, there are proteolytic ferments, some acting in acid, some in alkaline media. There is no doubt that such ferments co-operate with those in the body in the digestive process, both in the stomach and intestine. An enzyme capable of

digesting cellulose was not found. In cases of weak digestion in man, the administration of uncooked foods appears to be indicated.

W. D. H.

Digestion of Cellulose in, and Ferments of, the Cæcum. ARTHUR SCHEUNERT (*Zeit. physiol. Chem.*, 1906, 48, 9—26).—The alkaline contents of the cæcum in horse, pig, and rabbit is capable of dissolving cellulose in not unimportant quantities; the power is destroyed by boiling, but attempts to obtain the enzyme in the precipitate produced by alcohol failed. The quantity dissolved depends in part on the kind of cellulose used, the richness in micro-organisms, the length of time occupied in digestion, and the amount of the cæcal fluid. Even in the complete absence of micro-organisms, the fluid dissolves some cellulose, but if acid very little. Enzymes capable of dissolving cellulose do not appear to be present in the food swallowed; they are also absent from the secretion and from extracts of the mucous membrane of the cæcum and cæcal glands. The fluid contains a proteolytic, an amylolytic, a lactic acid producing, and an inverting enzyme, but no lipolytic enzyme. The secretion, or extracts, or expressed juice of the cæcal mucous membrane contain a weak amylolytic, but no proteolytic enzyme. Erepsin and entero-kinase are absent, but dextrose is converted into lactic acid. W. D. H.

Nitrogenous Metabolism in Normal Individuals. J. MOLYNEUX HAMILL and SAMUEL B. SCHRYVER (*Proc. Physiol. Soc.*, 1906, x—xii; *J. Physiol.*, 34).—In seven series of analyses of normal adults (laboratory workers) living in the usual way, the total nitrogen excreted in the urine varied from 9.6 to 16.5 grams daily; the relation of uric acid to this varied from 1.46 to 1.63 (average 1.54); the comparative constancy of this ratio is very noteworthy, so also is the relatively low value of the total nitrogen excreted. Great care is necessary in drawing conclusions as to sociological conditions from the amount of proteid consumed. Atwater's standard is 125 grams daily; in workhouses and prisons (reckoned from bought food), it varies from 134 to 177 (see Rowntree's *Poverty, a study in town life*); in the seven physiologists (reckoned from nitrogen excreted), it averaged 93 grams. W. D. H.

Lactic Acid in Intermediary Metabolism. ARTHUR R. MANDEL and GRAHAM LUSK (*Amer. J. Physiol.*, 1906, 16, 129—146).—Lactic acid disappears from the blood and urine in phosphorus poisoning when phloridzin glycosuria is induced. This indicates that lactic acid produced from proteid (whether in liver, intestinal wall, or elsewhere) is first synthesised to dextrose within the body before further distribution to the tissues. In phosphorus poisoning, this is followed by cleavage and a second production of lactic acid. But when diabetes is present, or when the mammary glands utilise dextrose to form lactose, then the cells affected become "sugar hungry" and attract fat in greater quantity than they can burn it (fatty infiltration).

There is a partial conversion of *D*-lactic acid, and there may be a

complete conversion of *d*-lactic acid, into dextrose in the diabetic organism.
W. D. H.

The Behaviour of Alkaline Earths in Metabolic Experiments with Caseinogen and Edestin. GOTTHELF MARCUSE (*Chem. Centr.*, 1906, i, 775; from *Verh. Ges. deut. Naturforsch. Aerzte*, 1904, ii, 492—493).—Feeding with proteids which contain phosphorus leads to better results than feeding on proteids which are free from that element. The excretion of magnesium is parallel to that of nitrogen, whilst that of calcium is independent of nitrogen elimination.
W. D. H.

Assimilation of Proteids in Animals. EMIL ABDERHALDEN and PETER RONA (*Zeit. physiol. Chem.*, 1906, 47, 397—403).—A further contribution to the question whether nitrogenous metabolism can be maintained by feeding dogs on the cleavage products of proteids. The dogs used were adults, but better conclusions would no doubt be drawn by the use of growing animals. Mixtures of amino-acids exercise a proteid-sparing influence, but certain members of the group are apparently not utilised; profuse diarrhoea, moreover, frequently occurs. The urine never contained amino-acids.
W. D. H.

Chemistry of Digestion. III. Proteid Decomposition in the Digestive Canal. E. S. LONDON (*Zeit. physiol. Chem.*, 1906, 47, 368—375. Compare Abstr., 1905, ii, 838).—Fischer's ester method gives good results for the analysis of the products of digestion of proteids found in the alimentary canal. In addition to the products previously described, alanine and aspartic acid can also be isolated.
W. D. H.

Fate of Leucine and Leucyl-leucine in the Organism of the Dog. EMIL ABDERHALDEN and FRANZ SAMUELY (*Zeit. physiol. Chem.*, 1906, 47, 346—353).—Racemic leucyl-leucine and racemic leucine were added to the food. Neither were found in the urine. Leucyl-leucine increases the excretion of urea; leucine has no effect on the total nitrogen or urea of the urine. It is possible that this is due to the insolubility of leucine. The faeces were not examined, except that they were found to contain an important amount of nitrogen. After subcutaneous injection of leucine, the urea increases in the urine.
W. D. H.

The Fate of Leucyl-glycine in the Organism of the Dog. EMIL ABDERHALDEN and BORIS BABKIN (*Zeit. physiol. Chem.*, 1906, 47, 391—393. Compare Abstr., 1905, ii, 839).—Leucyl-glycine is not split up by pancreatic juice (Fischer and Abderhalden), but if it is given by the mouth in dogs it is decomposed, and leads to an increase in the urinary urea. Neither the unchanged peptide nor amino-acids were found in the urine.
W. D. H.

The Behaviour of Certain Peptides towards Organ-extracts. EMIL ABDERHALDEN and YUTAKA TERUUCHI (*Zeit. physiol. Chem.*, 1906, 47, 466—470).—Glycyl-glycine and leucyl-glycine are not decomposed

into their constituent amino-acids by pancreatic juice, but they are so acted on by extracts of liver. It is believed that researches of this kind with extracts of organs may throw light on intermediary metabolism.

W. D. H.

Metabolism of Nucleic Acids in the Animal Organism.

EMIL ABDERHALDEN and ALFRED SCHITTENHELM (*Zeit. physiol. Chem.*, 1906, 47, 452—457).—Nucleo-proteids occupy an exceptional position among foods, for although their proteid component is broken down in the digestive tracts into simple cleavage products, it is not clear whether nucleic acid is resolved into its purine, pyrimidine, and carbohydrate constituents; the proteolytic ferments are certainly incapable of effecting this change. The discovery of nucleases renders it important to examine the question afresh. Pancreatic juice, whether activated by entero-kinase or not, soon dissolves sodium thymo-nucleate, but free purine bases are not found; gastric juice has practically no effect. One effect of the pancreatic action is to render the nucleate diffusible, but it is uncertain what change is produced. Extracts of pancreas and of the intestinal wall rapidly give a yield of purine bases. It therefore appears that the splitting of nucleic acid occurs by intra-cellular action after absorption.

W. D. H.

Proteid-sparing Action of Asparagine. MAX MÜLLER (*Pflüger's Archiv*, 1906, 112, 245—291).—The proteid-sparing action of asparagine described in herbivora has not been observed in carnivora. Zuntz considered this might be due to the bacteria of the paunch in ruminants decomposing the asparagine in preference to the proteid in the food. The present experiments show that *in vitro* the organisms do act in this manner, and apparently build up their proteid easily from simple substances. The proteid-sparing action of asparagine is thus a result of a kind of symbiosis.

W. D. H.

The Limit of Safety in adding Sulphurous Acid to Foods.

C. JACOBI and HEINRICH WALBAUM (*Chem. Centr.*, 1906, i, 1446—1447; from *Arch. exp. Path. Pharm.*, 54, 421—438).—The result of the experiments is such as to lead the authors to recommend the prohibition of the addition of sulphurous acid or sulphites as preservatives to foods.

W. D. H.

Influence of Temperature on Heart Beat.

T. BRAILSFORD ROBERTSON (*Biol. Bulletin*, 1906, 10, 242—248).—Arrhenius has shown that the velocity of a chemical reaction increases very much more rapidly with increasing temperature than any known physical phenomenon.

The rate of increase with rising temperature of certain biological phenomena, such as the heart beat and the development of eggs, is such as to prove that chemical reactions are involved, although not to the exclusion of possible concurrent physical changes. The present experiments on a heart of a crustacean (*Cerio daphnia*), which are described in full, support this view.

W. D. H.

Action of Barium Chloride on the Heart. EDUARDO FILIPPI (*Chem. Centr.*, 1906, i, 1501; from *Arch. Farm. sper.*, 5, 103—122).—Barium chloride poisons the heart muscle. A comparison between the action and that of digitalis is not tenable. W. D. H.

The Cause of Cessation of Rhythm in Isotonic Solutions of Non-electrolytes. A. J. CARLSON (*Amer. J. Physiol.*, 1906, 16, 221—229).—The duration of the activity of automatic tissues in isotonic solutions of sugar, urea, and glycerol depends on the condition of the tissues and the nature of the non-electrolyte, and not directly on the rate of diffusion of the electrolytes of the plasma in the inter-cellular spaces into the solution of the non-electrolyte. It is therefore in part due to some action of the non-electrolyte on the tissue. The cessation of the rhythm of the heart in such solutions cannot therefore be used as an argument in support of the view that the immediate cause of the rhythm of the heart is to be sought in the electrolytes of the plasma which surrounds it. W. D. H.

Physiology of Smooth Muscle. ANGELO MOSSO (*Mem. R. Accad. Lincei*, 1906, [v], 6, 1—26).—The retractile muscle of the penis exhibits the same spontaneous movements as do the smooth muscles of the bladder and blood-vessels of man, and it reacts towards psychical excitement by means of contractions similar to those observed in the blood-vessels and in the bladder. Experiments on the retractile muscle of the penis of the horse show that, even when the organs are separated from the body, carbon dioxide produces a contraction of the smooth muscles. The great vitality of the smooth muscles is shown by the fact that, when maintained in the air or in carbon dioxide at a temperature varying between 16° and 18—19°, they retain their excitability six days after death; they are able to contract under the influence of carbon dioxide even when putrefaction has commenced.

T. H. P.

Sugar Formation in the Isolated Liver. K. S. IWANOFF (*Chem. Centr.*, 1906, i, 574—575).—If the isolated liver of the rabbit is perfused with Locke's fluid, the sugar detected in the outflowing fluid is mainly dextrose; at the commencement only of the perfusion are maltose and isomaltose detected. The amount of sugar gradually decreases. It is increased by adrenaline, lessened by quinine. If the glycogen is previously mostly removed by fasting or perfusion with water, the amount of sugar obtained is small. The formation of sugar from glycogen is attributed to the action of one or more ferments. No evidence of the formation of sugar from fat or proteid was obtained.

W. D. H.

Contractility and Coagulation of the Colloids of the Ctenophore Swimming Plate. RALPH S. LILLIE (*Amer. J. Physiol.*, 1906, 16, 117—128).—A connection between contractile activity and coagulative changes in the colloids of the contractile tissue is indicated; the coalescence of colloid particles, as in other forms of coagulation,

for instance by heat, causes shortening; this is reversed during relaxation.

W. D. H.

Rapidity of Absorption of Odours by Milk. FRÉD. BORDAS and TOUPLAIN (*Compt. rend.*, 1906, 142, 1204—1205).—It is a well-known fact that milk is readily contaminated by odoriferous principles absorbed from the surrounding air, and control experiments conducted on the absorption of formaldehyde by milk show that milk which has been exposed for a few minutes to an atmosphere containing one part of formaldehyde in 100,000 readily gives the reactions of formaldehyde; in fact, the absorption is so rapid that milk can be used to detect in this way the presence of traces of formaldehyde in the air. M. A. W.

The Coagulation which occurs on Boiling Faintly Acid Milk. VON SOXHLET (*Chem. Centr.*, 1906, i, 579—580; from *Verh. Ges. deut., Naturforsch. Aerzte*, 1904, ii, 151—152).—At the commencement of souring of milk, boiling causes a coagulum; this occurs when only an eighth part of the acid is present which is necessary to produce coagulation at the ordinary temperature. It depends on the formation of an insoluble compound of caseinogen with soluble calcium salts. The acid first formed forms monocalcium phosphate from the dicalcium phosphate.

W. D. H.

The Amount of Lecithin in Milk. WALDEMAR KOCH (*Zeit. physiol. Chem.*, 1906, 47, 327—330).—The older methods for the estimation of lecithin in milk are not exact. Schlossmann's recent statement that lecithin is absent is, however, incorrect. If milk is freed from fat by the cream separator and treated with alcohol and then with ether, the addition of acetone to the ethereal solution causes a precipitate of lecithin and kephalin. This is dissolved in alcohol, and the kephalin removed by lead acetate. The solution is freed from lead by hydrogen sulphide, and then the cadmium compound of lecithin is obtained in small quantities. Whether the lecithin is free or in combination with caseinogen is undecided.

W. D. H.

Comparison of the Caseinogen of Various Milks. EMIL ABDEKHALDEN and ALFRED SCHITTENHELM (*Zeit. physiol. Chem.*, 1906, 47, 458—465).—The biological test (precipitin reaction) affords evidence that the caseinogen differs in the milk of different animals. The proportion of the various amino-acids obtained as hydrolytic products from the caseinogen of cow, goat, and woman is very similar, and the difference insufficient to support a theory of any great chemical difference between them.

W. D. H.

Reductases of Cow's Milk. E. SELIGMANN (*Chem. Centr.*, 1906, i, 772—773; from *Zeit. Hyg.*, 52, 161—178).—The reductase and peroxydase of cow's milk are not identical: oxydases are enzymes; peroxydase and reductase are products of bacterial activity.

W. D. H.

Excretion and Re-absorption in the Kidney. ADOLF BASLER (*Pflüger's Archiv*, 1906, 112, 203—244).—Sodium ferrocyanide introduced into the blood of a frog or rabbit very soon reappears in the urine. By treatment of the kidney from such animals with alcoholic ferric chloride, the microscope reveals prussian blue within the tubules, but where the excretion occurs is uncertain. Heidenhain's statement that indigo is excreted by the convoluted tubes is confirmed; the glomeruli are uncoloured. Sodium-carmin, on the other hand, is excreted mainly by the glomeruli; it is only when strong solutions are used that the epithelium of the tubules is slightly coloured. Much the same occurs with congo-red. When indigo solution is introduced into the kidney calyces, it passes in time into the tubules, but no re-absorption by their living cells occurs. Doing the same experiment with sodium ferrocyanide, this salt is shortly afterwards excreted by the other kidney; the same is true for sugar. The uses of Henle's loop are (1) to lengthen the tubule and increase the surface area of epithelium; (2) to increase the resistance to the glomerular outflow.

W. D. H.

Secretion of Urine. T. GREGOR BRODIE and WINIFRED C. CULLIS (*J. Physiol.*, 1906, 34, 224—249).—Dogs were killed by pithing, and sodium sulphate employed to produce diuresis. In these circumstances, the volume of urine secreted by a kidney working against a small ureter pressure was commonly greater than that secreted by the opposite kidney; the volume of sulphate secreted by the obstructed side was also usually in excess. The small ureter pressure employed did not lead to any changes in the blood-flow through the organ. If phloridzin was employed, the volume of urine and the amount of sugar were greater on the obstructed side. These results negative Ludwig's view of kidney action; they indicate that the glomeruli will secrete more water and probably more salt, and that the tubules excrete more salt when excited by a small ureter pressure. A saline diuretic excites greater secretory activity and does not work solely by causing changes in the blood and blood-flow.

W. D. H.

Secretion by the Frog's Kidney. WINIFRED C. CULLIS (*J. Physiol.*, 1906, 34, 250—266).—Nussbaum's statement that the renal artery in frogs supplies only the glomeruli has already been verified. The principle of artificial perfusion leads also to confirmatory results. Quite a simple operation is described in full by which an arterial perfusion, a venous perfusion *via* the renal portal vein, or both (that is, a total perfusion) may be obtained. By means of oxygenated saline (Locke's fluid), the necessary oxygen supply is kept up. Various diuretics were added to this. Phloridzin excites the tubule cells directly; they form dextrose and discharge it into the urine. Caffeine also excites the same cells; whether it also excites the glomeruli is still unsettled. With sodium sulphate, no flow of urine occurs unless the arterial circulation is present; it therefore acts as a specific stimulant to the glomerular epithelium. The chloride, nitrate, and phosphate of sodium act similarly. Dextrose acts in the same way, except that on a venous perfusion the kidney will also secrete; but

in these circumstances there is great delay in the starting of the secretion, and the secretion is very slow. Both glomerulus and tubules are concerned in the elimination of urea, but the relative importance of the two is not yet decided; strong solutions of urea kill the cells. The production of urine, both from the glomeruli and tubules, is a true secretory process; the glomerulus does not act as a filter, and re-absorption does not occur extensively within the tubules. The last conclusion depends largely on the analyses of the urine, which are given in detail.

W. D. H.

Secretion by the Frog's Kidney. FRANCIS A. BAINBRIDGE and ARTHUR P. BEDDARD (*Proc. Physiol. Soc.*, 1906, ix—x; *J. Physiol.*, 34).—An ordinary Nussbaum experiment fails to produce secretion, for the loss of oxygen due to tying the arteries leads to death and desquamation of the renal epithelium. This may be obviated by placing the frogs in nearly pure oxygen at atmospheric pressure. A secretion of urine then usually follows injection of urea, dextrose, phloridzin, or disodium hydrogen phosphate. The urine in all cases contained urea, chlorides, and sulphates, and is acid to phenolphthalein. After phloridzin, the urine reduces Fehling's solution. Uric acid or phosphates were not found in the urine either of these or of normal frogs.

W. D. H.

The Potassium in Human Urine in Altered Circulatory Conditions of the Kidney. FRIEDRICH WOHLWILL (*Chem. Centr.*, 1906, i, 1452; from *Arch. exp. Path. Pharm.*, 54, 389—397).—The urine of a young patient with orthostatic albuminuria was investigated. In the orthostatic periods the proportion K/Cl is doubled or more than doubled. This is mainly due to lessening of the chlorine; the acidity of the urine falls also. In a case of heart insufficiency, the same conditions were noted.

W. D. H.

Equilibrium in Solutions of Phosphates. LAURENCE J. HENDERSON (*Amer. J. Physiol.*, 1906, 16, 188—189. Compare this vol., ii, 185).—Both mono-sodium and mono-potassium phosphates are neutral to methyl-orange. In accordance with this, the behaviour of urine to methyl-orange does not prove that disodium and similar phosphates must be present. Folin's method for the determination of urinary acidity is recommended.

W. D. H.

Excretion of Inorganic Compounds. II. Barium. LAFAYETTE B. MENDEL and DUDLEY F. SICHER (*Amer. J. Physiol.*, 1906, 16, 147—151). **III. Rubidium.** LAFAYETTE B. MENDEL and OLIVER E. CLOSSON (*ibid.* 152—159. Compare *Abstr.*, 1904, ii, 357).—There is a close resemblance in the manner of excretion of barium and strontium salts. If barium chloride is introduced subcutaneously, it is eliminated for a few hours and to a slight extent only by the kidneys. It is eliminated to a larger extent by the fæces, but here again the actual amount is small, and excretion continues for a long time, and considerable quantities of the barium are deposited in the organism.

Rubidium chloride, on the other hand, resembles in its excretion salts

of lithium and cæsium. The elimination by the fæces is small, and that by the urine is much greater and continues for a long time, in some experiments for more than thirty days after an injection. The muscles form the principal situation where it is temporarily deposited in the body.

W. D. H.

Urobilin. F. FISCHLER (*Zeit. physiol. Chem.*, 1906, 47, 336—338).—Clinical experience is against the view that urobilin originates solely in the intestine. In the present research biliary fistulæ were made in dogs, so that no bile entered the intestine, and the animals were prevented by a wire muzzle from licking up the bile from the external orifice. Under these conditions the amount of urobilin in the fæces was very small, the bile contained scarcely any urobilin and very little urobilinogen; the urine contained neither. The administration of ethyl or amyl alcohol caused a large increase in the urobilin, and a small increase in the urobilinogen of the bile. Phosphorus poisoning did the same, so also did the administration of tolylenediamine. The amount of urobilin in the urine rose also, but that in the fæces remained at the previous low level. These experiments prove that the pigment can originate outside the intestine, probably in the liver. The dogs were icteric, and the blood contained bilirubin; the excretion of this into the intestine will explain the presence of a little urobilin there.

W. D. H.

The Amount of Amino-acids in Normal Human Urine. EMIL ABDERHALDEN and ALFRED SCHITTENHELM (*Zeit. physiol. Chem.*, 1906, 47, 339—345).—Free amino-acids do not occur in appreciable amount in normal urine. Their presence indicates a disorder of intermediary metabolism. From 10 litres of urine, 0.2 gram of β -naphthalenesulphoglycine were obtained, but it is doubtful if this is free or combined. The use of excess of alkali is necessary to obtain it, and it is possible the alkali may split off the glycine from a conjugated product. Hippuric acid, however, is hardly at all decomposed by this treatment. In one or two cases there was evidence of a still smaller amount of another amino-acid.

W. D. H.

Amino-acids in Normal and Pathological Urine. FRANZ SAMUELY (*Zeit. physiol. Chem.*, 1906, 47, 376—390).—The possibility of detecting amino-acids in urine by naphthalenesulphonic chloride and the presence of excess in certain diseases (gout, leucæmia) render the question important. A number of fresh analyses are given, and special attention is directed to glycine; in a case of gout and one of leucæmia there was a considerable increase. In pneumonia, there is no noteworthy departure from the normal, which averages 0.14 gram of naphthalenesulphoglycine in the dog's urine. Glycine is present in the urine of new-born children.

W. D. H.

Excretion of Allantoin in Thymus Feeding. W. M'LACHLAN (*Proc. Roy. Soc. Edin.*, 1906, 26, 95—105).—Allantoin is normally found in the urine of dogs on all diets. The administration of raw thymus causes a great increase. Boiled thymus produces a less

marked effect; allantoin, therefore, does not simply arise from the nucleins and purine substances. Liver and pancreas cause a less marked rise.

DIARMID NÖEL PATON in an addendum (*ibid.*, 106) shows that lymph glands produce a smaller effect than thymus, and a little greater effect than pancreas.

W. D. H.

Elimination of Creatinine. OLIVER E. CLOSSON (*Amer. J. Physiol.*, 1906, 16, 252—267).—Creatinine is a constant urinary constituent in man, dog, and cat; it is independent of the ingestion of creatine and creatinine, and forms a characteristic endogenous katabolic end-product. The amount excreted is pretty uniform in any individual, even although the diet is changed, and is, as Folin states, roughly dependent on the mass of the active body tissues.

W. D. H.

The Detection of Toxic Bases in Urine. FRIEDRICH KUTSCHER and ALFRED LOHMANN (*Zeit. physiol. Chem.*, 1906, 48, 1—8).—Liebig's extract of meat contains among other substances certain toxic bases such as methylguanidine and muscarine. Others recently described, novaine and oblitine, are not so poisonous as these, but kill mice and cats on subcutaneous injection. If the extract is given in this way, novaine is found in the urine, but not oblitine; if given by the mouth, oblitine is found in the urine, and novaine in the fæces. The method of separating such substances from the urine is described. Among other substances found in the urine was neurine. According to Marino-Zuco and Dutto, Addison's disease is a chronic choline poisoning, and choline, not neurine, is found in the urine. The much disputed question of the toxicity of the urine may be in part a question of diet, for Liebig's extract is much used as a food.

W. D. H.

The Amount of Cholic Acid in Human Fæces. FELIX VON OEFELE (*Zeit. öffentl. Chem.*, 1906, 12, 189—190. See this vol., ii, 501).

Glycogen in Pathological Cases. OSCAR LUBARSCH (*Chem. Centr.*, 1906, i, 771—772; from *Virchow's Archiv*, 183, 188—228).—The old statement that embryonic tissues contain more glycogen than the adult is confirmed by micro-chemical methods, but its presence in secretory organs and smooth muscle is not constant, and it is absent from certain tissues, for instance, bone, spleen, ovary, testis, lymph glands, blood, nervous tissues, and most connective tissues. In certain pathological conditions in the adult, the amount increases, but there is no relation between the deposition of glycogen and amyloid degeneration. It is present in tumours in which the cells are of the embryonic type. The source of the glycogen is believed to be carbohydrate and gluco-proteid material.

W. D. H.

Cystinuria. ARCHIBALD E. GARROD and WILLIAM H. HURTLEY (*J. Physiol.*, 1906, 34, 217—223).—In two cases of cystinuria referred to, no diamines were found in the urine, although previously both

patients had secreted them in the urine. Leucine and tyrosine were also absent. In one case, 5 grams of arginine carbonate were given by the mouth; this was not followed by the excretion of putrescine, although the patient had spontaneously excreted that substance five years previously; further, no tyrosine could be detected in the urine after a dose of 5 grams given by the mouth. The same patient frequently excreted small quantities of a substance which yielded a crystalline benzoyl compound melting at 205°, and was probably a derivative of tryptophan.

W. D. H.

A New Metabolic Product in the Urine in Severe Cases of Diabetes. KASIMIR STRYZYKOWSKI (*Chem. Centr.*, 1906, i, 583; from *Pharm. Post*, 39, 2—3).—This new abnormal product gave a green fluorescence on adding 5 per cent. of 40 per cent. formaldehyde to diabetic urine in thirteen cases out of forty. These were all severe cases. The solubilities and optical properties of the pigment so formed are described, but the chemical nature of the material is unknown.

W. D. H.

Sarcocactic Acid in the Cerebro-spinal Fluid in Eclampsia. H. FÜTH and GEORG LOCKEMANN (*Chem. Centr.*, 1906, i, 1452; from *Centr. Gynaekol.*, 1906, 41—43).—The cerebro-spinal fluid was removed in several cases of eclampsia by lumbar puncture and examined. The most important alteration noted was the presence of sarcocactic acid in greater amount than in either the blood or urine.

W. D. H.

The Poison of Eclampsia. ZWEIFEL (*Chem. Centr.*, 1906, i, 1503—1504; from *Münch. med. Woch.*, 53, 297—299).—In puerperal eclampsia, the urea excreted falls, the ammonia increases, the fully oxidised sulphur falls, and the incompletely oxidised sulphur rises. This indicates a general lessening of katabolic oxidation in proteids. Under similar conditions, Hoppe-Seyler found lactic acid in the urine. It is constantly found here, and is regarded as the poison of the condition.

W. D. H.

The Detection of Lactic Acid in the Blood, Urine, and Cerebro-spinal Fluid of Eclamptic Women. GEORG LOCKEMANN and H. FÜTH (*Chem. Centr.*, 1906, i, 1504; from *Münch. med. Woch.*, 53, 299—300).—Some estimations and the method employed are described. The lactic acid of the urine increases as the fits go on, but after four days it disappears, and the urine yields a crystalline substance of unknown nature.

W. D. H.

Physiological Effects of Certain Phosphorus Compounds on Milch Cows. W. H. JORDAN, EDWIN B. HART, and A. J. PATTEN (*Amer. J. Physiol.*, 1906, 16, 268—313).—This is a study of the nutritive relations and functions of the phosphorus compounds of cattle foods. The variation in phosphorus intake was mainly produced by admixture with the bran substance named phytin. The effect on the milk in milch cows was the chief object of the present investigation. The phosphorus reappears in inorganic compounds, especially in the

fæces, and to some extent in the urine. The effect on the milk is practically nil. The data given are very exhaustive, and further work is contemplated.

W. D. H.

Physiological Action of Magnesium Salts. III. Their Narcotising Effect on Nerve Fibres. SAMUEL J. MELTZER and JOHN AUER (*Amer. J. Physiol.*, 1906, 16, 233—251. Compare this vol., ii, 244).—Solutions of magnesium salts directly applied to nerve trunks never produce irritation, but cause a complete block to the passage of impulses; the more concentrated the solution, the more quickly does this effect supervene, but the time is slower than for other local or general anæsthetics. After removal of the solution, the effect disappears, and recovery is assisted by washing with Ringer's solution. Some nerves are more readily affected than others, for instance, sensory than motor. This is believed to be due to a difference of irritability of the nerve endings, and not to a selective action of the magnesium salts.

W. D. H.

Physiological Action of Lanthanum, Praseodymium, and Neodymium. B. J. DRYFUSS and CHARLES G. L. WOLF (*Amer. J. Physiol.*, 1906, 16, 314—323).—Solutions containing 0·8 per cent. of the chlorides of the above-mentioned elements coagulate the proteids of serum and egg-white. The addition of potassium citrate causes the precipitate to disappear. Proteoses and peptones are not precipitated. The poisonous action of the chlorides was tested on bacteria and other unicellular organisms, on blood corpuscles, on muscle and nerve, on the heart, and on the entire organism of frogs, birds, and small mammals. Very small daily doses, hypodermically administered, produce but little effect. Large doses (0·1 gram in a guinea pig) cause convulsions and death. Hæmorrhages and congestion were found in certain organs, especially the lungs. The general law regarding the toxicity, as tested by unicellular organisms, muscle, and nerve, is that equal molecular solutions increase in toxicity with increasing molecular weight. Part of the acute effect is due to hydrolysis of the salts and consequent toxicity of the acid produced.

W. D. H.

The Physiological Action of Formaldehyde. JULES JACOBSEN (*Chem. Centr.*, 1906, i, 693; from *Verh. deut. Naturforsch. Aerzte*, 1904, ii, 32).—The compounds of formaldehyde with indifferent organic substances such as lactose are free from caustic action. A dog received 32 grams of this compound; about a quarter was found in the urine as such, and a tenth as hexamethylenetetramine. The main amount of the remainder was decomposed into formic acid and carbon dioxide, and some was possibly united to proteid and circulated in the blood stream. Animals which received a mixture of diphtheria toxin and formaldehyde remained alive.

W. D. H.

Behaviour of Phenolphthalein in the Animal Organism. JOSEPH H. KASTLE (*Chem. Centr.*, 1906, i, 1559; from *Publ. Health and Marine Hosp. Service of the U.S. Hyg. Lab. Bulletin* No. 26, 23—29, 1906).—If phenolphthalein and other phthaleins (fluorescein, &c.)

are injected into the peritoneal cavity of guinea-pigs, a complex compound is excreted in the urine, which gives no colour with alkali, but yields phenolphthalein on decomposition with hydrochloric acid. *o*-Cresolsulphophthalein is found in large quantities unchanged in the urine, whereas phenolphthalein is only present in traces. Fluorescein is readily absorbed and more toxic. The complex compound alluded to above is soluble in alcohol, and hydrolysed by acid, by micro-organisms, by saliva, but not by liver extract. W. D. H.

The Behaviour of Digitoxin in the Organism. MAX CLOETTA and H. F. FISCHER (*Chem. Centr.*, 1906, i, 1369—1370; from *Arch. exp. Path. Pharm.*, 54, 294—313).—Animals of various kinds were poisoned with digitoxin, and the drug sought for in the organs and urine by methods which are fully described. It appears to have no special affinity for the heart or nervous tissues; the amount found in various parts is proportional to the amount of connective tissue present. No evidence that the heart muscle destroys digitoxin was found. Part of it passes slowly into the urine. The products of its decomposition are probably not cumulative in their action. W. D. H.

Physiological Actions of Ergot. HENRY H. DALE (*J. Physiol.*, 1906, 34, 163—206).—The effects of such preparations of ergot as cornutine and sphacelotoxine fall into two groups: (1) stimulant to plain muscle, especially in the arteries, uterus, and sphincter iridis, and (2) paralysis of the motor elements which adrenaline stimulates, the inhibitory elements retaining their normal function. It is probable that different active substances are responsible for these effects, and that the one which produces paralysis is also concerned in the central convulsant effects described by Kobert. Incidental conclusions in reference to the nerve supply of certain organs are also given. The pressor substance in the infundibular part of the pituitary body acts on some constituents of the plain muscular fibre other than that which is excited by adrenaline and by impulses reaching sympathetic nerve endings. W. D. H.

Intravenous Injection of Bone Marrow Extracts. ORVILLE H. BROWN and DON R. JOSEPH (*Amer. J. Physiol.*, 1906, 16, 110—116. Compare Abstr., 1905, ii, 745).—The effect of extracts of the bone marrow of pigs when intravenously injected is to produce on the blood pressure a depressor and a pressor effect. There appear to be two depressor and one pressor substances, which are separable by their solubilities and the relative duration of the effect. All these materials are soluble in boiling saline solution. Their chemical nature is unknown. W. D. H.

The Relation between the Fat and Carbohydrates of the Body in Phosphorus Poisoning. MOHR (*Chem. Centr.*, 1906, i, 694; from *Verh. deut. Naturforsch. Aerzte*, 1904, ii, 34—35).—In phosphorus poisoning there is a great diminution of the hepatic and body glycogen generally; it is used with the fat and proteid as additional fuel in

combustion processes. The fatty infiltration of the liver which occurs in this condition is believed to be reparatory. W. D. H.

Action of Poisons on Adult and Embryonic Funduli. TORALD SOLLMANN (*Amer. J. Physiol.*, 1906, 16, 1—46).—The action of cyanides, alkaloids, and other poisons are investigated in detail in relation mainly to the age of the funduli. W. D. H.

Toxicity of Methylatropinium Bromide, Homatropine Hydrobromide, Eumydrine, and Atropine Sulphate. ASTENORE BERTOZZI (*Chem. Centr.*, 1906, i, 1501; from *Arch. Farm. sper.*, 5, 123—133).—The fatal dose per kilo. in the rabbit for the drugs named in the above order when given intravenously is respectively 0.0296, 0.1387, 0.0211, and 0.1687 gram. There is a similar relative toxicity if the drugs are given hypodermically. W. D. H.

Action of Strychnine on the Spinal Cord. DAVID FRASER HARRIS and WILLIAM MOODIE (*J. Physiol.*, 1906, 34, 213—216).—The rate of strychnine spasms is differently given by various observers. This is accounted for by the fact that the rate varies with the time; at the onset it is most rapid, and the rate gradually falls during a convulsive attack. The experiments were made on frogs. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Apparatus for the Cultivation of Bacteria with High Oxygen Concentration and for the Determination of the Oxygen Maxima of the Bacteria and the Periods at which they are Killed at Higher Oxygen Concentrations. ARTHUR MEYER (*Centr. Bakt. Par.*, 1906, ii, 16, 386—398. Compare Abstr., 1905, ii, 848).—The apparatus described, with sketches, consists of a compressed gas cylinder with connecting tube, an autoclave for use with compressed gas, and manometers for pressures below 5 kilos. and 2 kilos.
N. H. J. M.

Bacteriological Investigations in the Acetic Acid Factory. WILHELM HENNEBERG (*Chem. Centr.*, 1906, i, 613—614; from *Deut. Essigind.*, 9, 393—395, 403—405, and 410—412).—The microscopical examination of beech shavings from acetic acid vats showed the presence of extremely large numbers of acetic acid bacteria, and that their position in the fibre prevents their being washed out by the acetic acid in passing through. The acetic acid from vats in good order is characterised by containing only few bacteria, whilst the acid from unhealthy vats contains large numbers of organisms—infusoria, *Dematium*, *B. xylinum*, &c.

The examination of a number of samples of wood shavings showed that *B. xylinum* was invariably present. It is evidently harmless.

N. H. J. M.

Action of Charlock on Nitrification. E. GUTZEIT (*Centr. Bakt. Par.*, 1906, ii, 16, 353—381).—The injurious effect of charlock is not confined to the direct withdrawal of water and manurial substances required by the crop, but is partly attributed to diminished nitrification due to the removal of lime and water.

Charlock can be destroyed by a single application of iron sulphate.

N. H. J. M.

Utilisation of Peat Holes for the Intensive Production of Nitrates. ACHILLE MÜNTZ and E. LAINÉ (*Compt. rend.*, 1906, 142, 1239—1244. Compare this vol., ii, 114).—Peat as a medium for nitrifying organisms is far superior to other soils rich in organic matter, and the rate of formation of nitrates in such a medium is 1000 times greater than that hitherto obtained (compare Boussingault, *Abstr.*, 1873, 725; 1877, 735).

When a 0.75 per cent. solution of ammonium sulphate is passed over a peat-bed impregnated with nitrifying organisms, it becomes charged with nitrates to the extent of 0.82 per cent.; this can be increased to 4.17 per cent. by adding a further quantity of ammonium sulphate to the solution and again subjecting it to the nitrifying action, the operation being repeated five times. The most suitable temperature for the reaction is 30°, and the fuel necessary for maintaining this temperature is afforded by the air-dried peat. Further, the nitrogen contained in the peat, which amounts to 2 to 3 per cent., can be obtained in the form of ammonia to the extent of 1.79 to 1.612 per cent. by distilling the peat in superheated steam, the other products of the distillation (hydrocarbons, water gas, tar, &c.) forming the fuel required for the operation. Peat, therefore, is singularly well adapted for the intensive production of nitrates, since it forms an excellent medium for the growth of the organism, supplies the fuel necessary for the various operations, and finally supplies the ammonia required for the production of nitrates.

M. A. W.

Bacteriological Investigation of Soils. BUHLERT and FICKENDEY (*Centr. Bakt. Par.*, 1906, ii, 16, 399—405).—The soil (300—500 grams) is shaken vigorously for five minutes with an equal weight of sterilised tap-water, and is then ready for inoculation. For nitrification and nitrogen assimilation, 20 c.c. are employed, and for denitrification and peptone decomposition 5 c.c. Three inoculation experiments generally suffice, and the mixture is shaken each time before the required amount is taken out with a pipette.

Experiments with five different soils showed that after aëration the power of producing ammonia from peptone was slightly less than when not aerated; nitrification was also generally diminished by aëration. Denitrification and nitrogen assimilation were, however, more active in the aërated soil. As regards denitrification, it is of course not to be supposed that under natural conditions mechanical operations will

result in an increased loss of nitrogen. It is probable that the effects of aëration will vary according to circumstances, possibly according to the degree of aëration.

N. H. J. M.

Formation of Crystals in Cultures of Denitrifying Bacteria. H. B. HUTCHINSON (*Centr. Bakt. Par.*, 1906, ii, 16, 326—328).—Cultures of bacteria from garden soil in Giltay solutions produced skins consisting of acicular crystals of magnesium phosphate and became strongly alkaline. Denitrification was not vigorous. The alkalinity, which is presumably due to production of sodium carbonate from the citric acid, became equal to that of a $N/10$ solution in four weeks.

The alkalinity and the amount of crystals seem to increase with increased surface and aëration.

N. H. J. M.

Nutrition of Wood-destroying Fungi. BASILIUS MALENKOVIĆ (*Centr. Bakt. Par.*, 1906, ii, 16, 405—416).—Experiments with *Coniophora cerebella* showed that it is able to consume nearly all the substances which are to be obtained from wood. When wood is attacked, more substance is destroyed than is utilised for the nutrition of the fungus, and it is improbable that any one constituent of the wood is completely consumed.

N. H. J. M.

Formation of Hydrogen Sulphide in Mineral Waters. THOMANN (*Chem. Centr.*, 1906, i, 579; from *Schweiz. Woch. Pharm.*, 44, 5—6).—Experiments by Goslings have shown that the formation of hydrogen sulphide in bottled mineral waters must be attributed to the presence of micro-organisms; in Passug water an anaërobic spirillum which reduces sulphates has been detected.

P. H.

Adaptation of Yeast to Sulphurous Acid. GILBERT GIMEL (*Chem. Centr.*, 1906, i, 864; from *Bul. Assoc. Chim. Sucr. Dist.*, 23, 669—672).—The adaptation of yeast to sulphurous acid manifests itself in the increase of oxidising power. The presence of potassium carbonate is favourable, whilst monocalcium phosphate is not. A combination of sulphur dioxide with the yeast cells takes place, since the percentage of sulphur dioxide in the ash of acclimatised yeast is much greater than in ordinary yeast.

The employment of adapted yeast is necessary in the case of mashes containing sulphurous acid, such as grape and molasses mashes.

N. H. J. M.

Influence of Colloids on the Secretion and Action of Invertase. ENRICO PANTANELLI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 377—385).—In a previous publication (*Annali Bot.*, 1905, 113—142) the author showed that gum arabic, gelatin, and peptone have a markedly favourable influence on the development of *Mucor stolonifer* and of a race of yeast isolated from Roman bread and an Ellipsoideus yeast from Chianti wine, that both the internal and external invertive activity are notably diminished by gum and peptone, whilst gelatin seems to be without action, and that with the above yeasts the permeability of the protoplasts towards invertase varies along with the permeability

for certain salts, such as sodium and ammonium chlorides and magnesium sulphate, and for sugar. The permeability has, indeed, its maximum value when the fermentative activity is at its highest, and is considerably diminished by the above-named colloids, especially by gum and peptone.

Colloidal silica, $\text{Si}(\text{OH})_4$, also impedes the secretion of invertase, but not always its intercellular production.

As the age of the cells increases, the extra-cellular invertive activity also undergoes increase, which, in the case of yeasts, corresponds with the augmentation of permeability due to the action of the alcohol and other products of fermentation, including the carbon dioxide; like certain injurious substances, the latter produces a marked increase in the permeability. In *Mucor*, also, the secretion of invertase increases with the age of the culture, owing to the action of the products of change excreted and to the insufficient aëration of the submerged portion of the mycelium.

With yeast cells, the amount of invertase reaches a maximum at the beginning of the development and then falls both inside and outside the cell if the surrounding liquid is free from colloids. In presence of the latter, it also reaches a maximum inside the cells at the commencement of fermentation, but outside the cells the maximum is attained at a later stage. This indicates that the secretion of invertase is not merely a function of the active surface. The facts that sucrose disappears more quickly than the invert sugar increases and that the latter disappears only slowly indicate that, especially in the early days, the sucrose is absorbed as such by the yeast.

With *Mucor stolonifer* and *M. mucedo*, the internal invertase reaches a maximum at about the sixth day in cultures on a non-colloidal substratum, whilst it increases gradually but continuously with age in presence of colloids. In both cases, the external invertase increases continuously, although it is always in small amount.

The unicellular mycelium of *Phycomyces nitens* behaves similarly to that of *Mucor*, but multicellular mycelia, such as those of *Penicillium glaucum* and *Botrytis cinerea*, exhibit certain deviations in their action.

T. H. P.

Action of Various Reagents on Amœba Cultures. J. B. THOMAS (*Chem. Centr.*, 1906, i, 863; from *Dep. Int. Bureau Gov. Lab. Manila*, 1905, No. 32, 17—29).—Boric acid, eucalyptol, cassia oil, ichthyol, and infusion of quassia have hardly any action on the growth of amœbæ. Tannic acid (1 per cent.), copper sulphate (1:2000), potassium permanganate (1:2000), quinine sulphate (1:500), silver nitrate (1:2000), argyrol (1:500), protargol (1:500), hinder their growth within half an hour.

W. D. H.

Organic Acids as a Source of Carbon for Algæ. O. TREBOUX (*Chem. Centr.*, 1906, i, 770; from *Ber. Deut. Bot. Ges.*, 23, 432—441).—Forty different species of algæ have been cultivated in a sterilised solution of ammonium sulphate, dipotassium hydrogen phosphate, magnesium sulphate, potassium sulphate, and ferrous sulphate to which 0.05 or 0.1 per cent. of one of the following acids

was added: formic, acetic, propionic, lactic, butyric, valeric, oxalic, succinic, malic, tartaric, and citric acids. The potassium or ammonium salt was used, and in some cases the amino-acid, but when either of the two latter was added the ammonium sulphate was omitted from the culture solution. Twenty species of algæ were found to be able to derive the carbon required for growth from an organic acid. It was remarkable, however, that in nearly all cases acetic acid was the only acid assimilated, whilst the acids which had longer carbon chains, and the constitution of which therefore approached more nearly that of sugar, were not attacked. Lactic acid was assimilated by two species and butyric and citric acids each by one. The growth of some algæ was but slightly less when ammonium salts of the acids were used instead of ammonium sulphate and potassium salts; other kinds were apparently affected by the ammonia liberated by the consumption of acid. The amino-acids proved less suitable; ammonia was also formed by the assimilation of the acids. The experiments show that even from the physiological point of view there is no sharp line of demarcation between moulds and green plants in regard to nutrition, and that all the organic substances which are required for the creation of the cell may be derived from an organic acid. E. W. W.

Culture Researches with *Aspergillus niger* and Certain Amino-acids and Peptides. EMIL ABDERHALDEN and YUTAKA TERUUCHI (*Zeit. physiol. Chem.*, 1906, 47, 394—396).—Various amino-acids form good nutrient material for moulds. In the present research, *Aspergillus niger* was grown on a medium to which various peptides were added, and the amount of mould obtained at the end of given time weighed. Glycine, glycyl-glycine, and triglycine were found to be well utilised; glycyl-alanine, leucyl-glycyl-glycine, and aminobutyrylaminobutyric acid were the least favourable. In most cases oxalic acid was found, the amount of which is regarded as a measure of intensity of growth. W. D. H.

Mould Fungus which Decomposes Paraffin. OTTO RAHN (*Centr. Bakt. Par.*, 1906, ii, 16, 382—384).—The fungus is a variety of *Penicillium*. In addition to paraffin, it grows well on palm fat agar and on stearic acid, but not on yellow vaselin. The paraffins employed melted at 45° and at 56°, and were carefully purified. In two experiments with 877 and 861 mg. paraffin, 79.1 and 77.1 per cent. respectively was decomposed in six weeks. N. H. J. M.

Sterilisation of Air by means of Ozone. DONATIEN LABBÉ (*Chem. Centr.*, 1906, i, 695; from *Rev. gén. Chim. appl.*, 1905, 8, 387—389).—The addition of 10 mg. of ozone to every cubic metre of air renders the air perfectly sterile. P. H.

Poisonous Action of Formic Acid on Different Fungi. WILHELM HENNEBERG (*Chem. Centr.*, 1906, i, 694—695; from *Zeit. Spiritus-ind.*, 29, 34—35).—The numbers given are the percentages of formic acid in which various micro-organisms failed to develop. Hay bacilli, 0.04; acetic acid bacteria, 0.06; lactic acid bacillus,

0.15 ; and yeast, 0.2. The resisting power of yeast could doubtless be increased so as to make it possible to employ formic acid as an antiseptic in yeast factories, &c. N. H. J. M.

Toxicity of Phenol compared with that of other Substances. THOMAS BOKORNY (*Chem. Zeit.*, 1906, 30, 554—556).—The toxic action of a number of different substances at various dilutions has been studied on algæ and moulds, and the following lethal doses have been determined. Ten grams of yeast are killed by 0.05—0.1 gram of phenol, 0.02—0.04 gram of formaldehyde, 0.5 gram of *o*-hydroxybenzaldehyde, or 0.2—0.4 gram of acetic acid. The author is of opinion that the limit of dilution at which a particular substance will exert its toxic action is dependent on the dilution at which the chemical reaction between the poison and the proteid of the living cell will take place. P. H.

Action of Alkalis on the Development of Plants. ALBERT EINECKE and THEODOR PFEIFFER (*Chem. Centr.*, 1906, i, 585—586; from *Verh. Ges. deut. Naturforsch. Aerzte*, 1904, ii, 171—172).—Calcium-zeolites fix potassium manures and ammonium sulphate. Sodium chloride always increased the growth of the plants; the highest yields were obtained with small amounts of a mixture of sodium and potassium chlorides. It is probable that sodium can take the place of potassium to a great extent. N. H. J. M.

Separation of Acids by Roots and Mould Hyphæ and its Signification. GUSTAV KUNZE (*Chem. Centr.*, 1906, i, 1557; from *Jahrb. wiss. Bot.*, 42, 357—391).—The acid secreted by 180 seedlings of garden balsam has been estimated by titration with decinormal potassium hydroxide solution; a quantity of acid equivalent to 0.5 mg. of formic acid was found to be present. The acid reaction of the secretion is probably due to the presence of organic acids formed as intermediate products in the process of respiration. The liquid gave the reaction for sulphuric acid fairly distinctly, but the presence of phosphoric acid appeared doubtful. The elimination of carbon dioxide by the roots was proved, but the colour reactions obtained in the experiments could not have been caused by carbonic acid.

Since the corrosive action of the plants on marble, wollastonite, and potassium-lead glass was observed even when the plants did not form a distinctly acid secretion, the corrosion must be caused by the action of carbon dioxide; the plants did not attack feldspars. A leucite-basalt which had been acted on by cultures of *Penicillium* was found after calcination to contain 7 per cent. more of substances which were soluble in acetic acid than the mineral which had not been in contact with the mould. All the solutions contained potassium, calcium, magnesium, iron, traces of chlorine and phosphoric acid. E. W. W.

Probable Causes of the Differences in the Relations between the Nutrition of Leguminous and Gramineous Plants. OTTO LEMMERMANN (*Chem. Centr.*, 1906, i, 586; from *Verh. ges. deut. Naturforsch. Aerzte*, 1904, ii, 145).—Gramineous plants

evaporate more water than *Leguminosæ*, and hence take up more soluble matter from the soil. Leguminous plants can do without the combined nitrogen in the soil, and by means of their extensive root systems and greater root acidity are able to obtain mineral matter which is out of the reach of gramineous plants. N. H. J. M.

Formation of Different Respiration Enzymes depending on the Stage of Development of the Plants. WLADIMIR PALLADIN (*Chem. Centr.*, 1906, i, 1441; from *Ber. deut. bot. Ges.*, 24, 97—107).—It was shown previously (*Ber. deut. bot. Ges.*, 23, 240) that the preponderance of one or another respiration enzyme depends on the degree of development of the plant. Anaërobic respiration predominates in the embryonal organs and diminishes with the progress towards active life. Oxydase is almost completely absent in the embryonal organs.

The relation of the carbon dioxide of anaërobic respiration to that of oxygen respiration (J/N) was found to be as follows in the frozen plants examined: wheat germs = 1; etiolated bean leaves = 0.42 and 0.41; the same with sugar = 0.33; the same after sugar and exposure to green light = 0.23; old leaf of *Plectogyne japonica* = 0.71.

N. H. J. M.

Effect of Impregnating with Nutritive Salts on the Germination of Seeds. O. KAMBERSKÝ (*Chem. Centr.*, 1906, i, 570—571; from *Zeit. landw. Versuchswes. Oesterr.*, 9, 33—43).—Contact of seeds for forty-eight hours with a solution containing equal amounts of ammonium nitrate, potassium nitrate, hydrogen diammonium phosphate, and hydrogen disodium phosphate, as proposed by Iszleib (*Deut. landw. Presse*, 1904, No. 84), resulted in retarded germination, except in the case of beet, and in a lower germination percentage. Rust and mould fungi were not injured by the treatment. N. H. J. M.

Effect of Calcium Cyanamide on the Energy of Germination. BARTSCH (*Chem. Centr.*, 1906, i, 585; from *Verh. Ges. deut. Naturforsch. Aerzte*, 1904, ii, 166—167).—Experiments in pots containing 8 kilos. of soil, of which one-third received 2 grams of calcium cyanamide, showed that the germination of mustard, oats, and barley was diminished when the seeds were sown immediately. The injurious effect was also noticed when the seeds were sown a week later, but was lessened in the case of barley. After an interval of three weeks, the manure had no injurious action. N. H. J. M.

A Green Organ devoid of Assimilatory Power. JEAN FRIEDEL (*Compt. rend.*, 1906, 142, 1092—1093).—The ovary of *Ornithogalum arabicum* has an intense blackish-green colour, and examination of a section shows that it contains an abundance of chlorophyll bodies, which have a black tint towards the periphery. On exposure to atmospheric air, the ovary does not assimilate carbon dioxide, although it respire vigorously; thus, in the course of four and a half

hours, the carbon dioxide content of air surrounding a single ovary rose to 6·4 per cent.

The leaf of *Ornithogalum arabicum* and the ovary of a related species, *O. umbellatum*, assimilate normally when exposed to air containing carbon dioxide.

It is suggested that the abnormal behaviour of the ovary of *O. arabicum* may be due to an alteration of the peripheral chlorophyll bodies, so that they do not assimilate, and in addition act as a screen preventing assimilation by the normal chlorophyll bodies of the interior of the ovary.

T. A. H.

Argemone Seeds from Curaçoa. W. H. BLOEMENDAL (*Chem. Centr.*, 1906, i, 1556; from *Pharm. Weekblad*, 43, 342—346).—Seeds of *Argemone albiflora*, *A. speciosa*, *A. grandiflora*, *A. hispida*, and *A. Hunnemannii* from Curaçoa, Cape Verde, and St. Eustatius yielded about 37 per cent. of a fatty oil. The oil extracted from *A. speciosa* by means of carbon tetrachloride had sp. gr. 0·9435 at 15°, iodine number 113·3, and saponification number 200·2, and gave a deep red coloration with nitric acid. An alkaloid was present in small quantity, but it was not identified with morphine.

E. W. W.

Crystals in Herba Conii. TUNMANN (*Chem. Centr.*, 1906, i, 478; from *Pharm. Zeit.*, 50, 1055—1057).—Leaves of *Conium maculatum*, which had been immersed in alcohol, were found to contain well-formed, rhombic needles and prisms of a yellow or orange-red colour, but sometimes nearly colourless, probably a dye of the carotin group. They occur chiefly in the lower epidermis, and also in the mesophyll and nerve vessels.

N. H. J. M.

Carotin Crystals [in Herba Conii]. TUNMANN (*Chem. Centr.*, 1906, i, 478—479; from *Pharm. Zeit.*, 51, 18).—Alcohol (70—90 per cent.) dissolves the green colouring matter in conium plants, whilst a portion of the yellow colouring matter often separates in the form of xanthocarotin crystals. The latter does not always crystallise in the original cells, but frequently passes in solution to portions of the plant free from chlorophyll and then crystallises. Numerous other plants were similarly treated, but none of them showed crystals of carotin.

N. H. J. M.

Composition of Lemon Juice. HEINRICH LÜHRIG (*Zeit. Nahr. Genussm.*, 1906, 11, 441—445).—The following average results were obtained on the analysis of ten samples of the juice pressed from fruit in the author's laboratory: total solids, 10·181; citric acid (anhydrous), 7·568; ash, 0·364; nitrogen, 0·059; invert sugar, 1·572; glycerol, 0·220; phosphoric acid, 0·023 per cent. The alkalinity of the ash corresponded with 4·99 c.c. of N/1 acid per 100 c.c. of juice.

W. P. S.

Fatty Oil from the Seeds of Manihot Glaziovii. GEORG FENDLER and O. KUHN (*Chem. Centr.*, 1906, i, 768—769; from *Ber. deut. Pharm. Ges.*, 15, 426—429).—The seeds of *Manihot Glaziovii*

contain 9.94 per cent. of fat, and the kernels and pods respectively 5.18 and 6.66 of water and 35.20 and 1.31 of substances extracted by ether. The greenish-yellow oil extracted by means of ether has an odour which resembles that of olive oil and a somewhat harsh and bitter taste; it forms clear solutions in ether, chloroform, benzene, carbon disulphide, acetone, amyl alcohol, &c., but becomes turbid on the addition of light petroleum and is not miscible with absolute alcohol or glacial acetic acid. The oil becomes turbid at 4°, but does not solidify at -17°; it has a sp. gr. 0.9258 at 15°, acid number 2.18, saponification number 188.6, Reichert-Meissl number 0.7, iodine number 137.0, and refractometer number 62.9 at 40°, and contains 10.6 per cent. of glycerol and 0.9 of compounds which cannot be saponified. It does not give the elaidin test. The oil dries at 55° in about ten hours, but only in several weeks at the ordinary temperature. The fatty acids, which consist of 10.97 per cent. of solid acids melting at 54° and 89.03 of liquid acids, have a mean molecular weight of 280.7; the mixture melts at 23.5°, solidifies at 20.5°, has a sp. gr. 0.8984 at 25°, acid number 197.6, saponification number 200.1, acetyl acid number 179.9, acetyl saponification number 200.6, alcohol number 20.7, and iodine number 143.1. The iodine number of the liquid acids is 163.6.

Manihot oil may possibly find a technical application in the manufacture of soap. E. W. W.

Comparative Studies on Three Species of Papaver. VITTORIO PAVESI (*Chem. Centr.*, 1906, i, 690; from *Atti R. Ist. Bot. Univ. Pavia*, 1906, 9).—Rheadine was obtained from the plants by stirring up the finely-powdered substance with milk of lime, allowing the mixture to dry in the air for two to three days, and then extracting with ether. The alkaloid was then removed from the ether by means of a solution of sodium tartrate, from which it was subsequently precipitated by ammonia. Rheadine forms thin, doubly-refracting needles, which darken at 238—240° and melt at 245—247° (compare Hesse, *Annalen*, 1866, 140, 146); it is slightly soluble in 95 per cent. alcohol, but rather more so in benzene or warm amyl alcohol; it forms a platinichloride of the formula $(C_{21}H_{21}O_6N)_2 \cdot H_2PtCl_6 \cdot 2H_2O$. *Rheagenine*, which, when crystallised from alcohol, melts at 235—237.5°, appears from its index of refraction to be isomeric with rheadine. Rheagenine is rather more soluble in alcohol than rheadine, and on treatment with bromine water or hydrobromic acid yields a more stable tribromide than the latter. Both substances give the same colour reactions.

Papaver Rhæas contains traces of meconic acid. *Papaver dubium* may be readily distinguished from *Papaver Rhæas* by its containing aporhein. *Papaver hybridum* contains the merest traces of another alkaloid in addition to rheadine. P. H.

Composition of Tamarind Pulp. OCTAVE REMEAUD (*J. Pharm. Chim.*, 1906, [vi], 23, 424—430).—Samples of commercial “crude” and “purified” pulps were analysed and compared with pulp prepared by the author from fruits collected at Saigon. The principal constituents found were tartaric acid, potassium hydrogen tartrate,

invert sugar, sucrose, and pectin. The "dry extract" ranged from 62.8 to 73 per cent., ash from 2.8 to 3.2 per cent., and "total acidity," calculated as tartaric acid, from 11.7 to 15.8 per cent.

T. A. H.

Medicinal and Useful Plants of Brazil. THEODOR PECKOLT (*Chem. Centr.*, 1906, i, 250—251; from *Ber. deut. pharm. Ges.*, 15, 183—202. Compare Abstr., 1904, ii, 142, 764; and 1905, ii, 113).—The amounts of water, ash, and of various organic constituents were determined in the following varieties of *Euphorbiaceæ*: *Phyllanthus niruri*, *Hieronyma alchorneoides*, *Croton echinocarpus*, *C. compressus*, *C. campestris*, *C. lobatus*, *Julocroton fuscus*, *Johannesia princeps*, and *Hevea brasiliensis*. The last is the most important source of india-rubber.

N. H. J. M.

Medicinal and Useful Plants of Brazil. THEODOR PECKOLT (*Chem. Centr.*, 1906, i, 769—770; from *Ber. deut. pharm. Ges.*, 16, 22—36. Compare Abstr., 1904, ii, 142, 764; 1905, ii, 113).—The abstract contains a detailed description of the amounts of various substances in the following plants: *Manihot utilissima*, *Manihot utilissima* var. *Cambaia*, *Manihot palmata*, *Manihot Glusiovi*, *Ricinus communis* var. *brasiliensis*, *radius*, *genuinus*, and *microcarpus*.

E. W. W.

Amount of Proteid in Barley, and Potassium Manuring. OTTO REITMAIR (*Chem. Centr.*, 1906, i, 154; from *Zeit. landw. Versuchsves. Oesterr.*, 8, 983—1014. Compare Abstr., 1903, ii, 177).—Application of potassium manure resulted in increased yields of grain, sometimes very considerable. The amount of proteids was not reduced. The quality of barley depends less on manuring than on other conditions.

N. H. J. M.

Nutrition of Barley with Potassium with Reference to its Quality. E. WEIN (*Chem. Centr.*, 1906, i, 780—781; from *Zeit. ges. Brauw.*, 29, 26—32).—The application of potassium, phosphoric acid, and nitrogen in soluble forms improves the quality of barley, or, if the quality is already satisfactory, increases the yield. The crop requires plenty of manure, especially when the plants are young. Potassium should therefore be applied even to good soils; small amounts suffice if given in conjunction with plenty of dung. Kainite is preferable to 40 per cent. potassium salts, except in the case of heavy soils.

N. H. J. M.

Composition of the Seed of Sugar Beet. FRIEDRICH STROHMER and O. FALLADA (*Chem. Centr.*, 1906, i, 1440—1441; from *Oesterr.-ung. Zeit. Zucker-Ind. Landw.*, 35, 12—22).—The fresh seeds contained 9.66 per cent. of water. The composition of the dry matter free from sand was as follows: nuclein, 3.16; proteid, 17.25; amides, 5.76; glycerides, 17.82; phytosterol (cholesterol), 0.96; lecithin, 0.46; starch, 19.58; pentoses, 3.03; crude fibre, 1.9; oxalic acid, 0.39; and ash,

4.99 per cent., including K_2O , 1.09; CaO , 0.23; and P_2O_5 , 2.70 per cent.

No sucrose or other reducing sugar was detected. N. H. J. M.

Chemical Composition of the Whey and Curd during the Manufacture of Emmentaler Cheese. G. KOESTLER (*Milchw. Zentr.*, 1906, 2, 193—224).—The paper deals with the changes which take place in the constituents during the making and ripening of this class of cheese. The addition of rennet to the mixture of milk and ripened milk causes an increase in the soluble nitrogenous substances, and the inclusion of these substances in the curd can be accomplished by the methods employed in the manufacture; this is of importance, as they probably play an important part in the subsequent fermentation of the cheese. At the commencement of the curdling, the proteid and fatty content of the whey decreases, but towards the end of the manufacture the amount of fat in the whey increases. The total amount of ash in the whey decreases, but the soluble ash increases as compared with the insoluble ash. The amount of calcium and phosphoric acid diminishes, calcium phosphate being removed from the whey during the heating of the cheese, whilst the composition of the curd (calcium phosphate, paracasein) shows no alteration during the ordinary working. The addition of rennet imparts a coagulating power to the whey, which remains constant during first operations, but vanishes during the heating of the curd. The cause of the rapid increase in the acidity of the whey after the removal of the curd may be due to concentration and to lactic acid fermentation, which is favoured by the presence of the soluble proteids. W. P. S.

Absorption of Phosphates by Soils. OSWALD SCHREINER and GEORGE H. FAILYER (*J. Physical Chem.*, 1906, 10, 239—263).—The authors have made experiments on the absorption of phosphates from solutions of monocalcium phosphate and disodium phosphate, and also on the removal of the absorbed phosphates by water, in the case of four types of soils—a clay, a loam, a sandy loam, and a fine sand. The results for the absorption are in accord with the differential equation, $dy/dv = K(A - y)$, where A is the maximum amount which the soil can take up, y is the amount taken up when volume v has passed through the soil. For the removal, the equation $dy/dv = K(y - B)$ is in accord with the experiments, B being the quantity of phosphate not removable from the soil by a reasonable quantity of water. The experimental values of y only approached near to A in the case of the sand, and the values of the constants appear to be the same for the two phosphates examined in the case of the clay and loam, but were different in the sandy loam and sand. L. M. J.

Destruction of Nematodes by treating the Soil with Carbon Disulphide and its Effect on Sugar Beet. HERMANN WILFARTH, HERMANN ROEMER, and GUSTAV WIMMER (*Chem. Centr.*, 1906, i, 492—493; from *Zeit. Ver. Rübenzucker-Ind.*, 1906, 1—18).—Treatment of the soil for three days with carbon disulphide completely destroyed the nematodes.

As regards the effect of nematodes on the plants, it was found that, as compared with normal roots, the following amounts of different constituents were withdrawn: nitrogen, 59.6; K_2O , 70.87; MgO , 44.5; and P_2O_5 , 70.87 per cent. The assimilation of sodium was diminished by only 13.35 per cent. in the root and increased by 5.26 per cent. in the leaf. Calcium assimilation was increased. The amount of sugar in the dry matter increased, owing, probably, to nitrogen being deficient.

N. H. J. M.

Action of Carbon Disulphide on Lower Vegetable Organisms and its Importance for the Fertility of Soils. BERTHOLD HEINZE (*Centr. Bakt. Par.*, 1906, ii, 16, 329—358).—The immediate effect of carbon disulphide in the soil is to suppress the production of amides and ammonia by putrefactive processes, and also nitrification; at the same time, the conditions become favourable to nitrogen-fixing organisms, especially *Azotobacter*. Subsequently, there is increased conversion of proteids and other organic nitrogen compounds into amides and ammonium compounds, whilst nitrification is resumed with increased vigour.

As regards other effects of carbon disulphide, it is noticed that soil so treated retains more moisture during a prolonged drought than untreated soil. Fallow soil treated with carbon disulphide remained practically free from weeds.

N. H. J. M.

Amount of Chlorine in Rain-water. WILLEM P. JORISSEN (*Chem. Centr.*, 1906, i, 698; from *Chem. Weekblad*, 1906, 3, 42—43).—As a result of ninety-two experiments, the author has found that, in certain districts near the North Sea, the mean proportion of chlorine in rain-water is about 29.6 mg. of chlorine per litre.

P. H.

Amounts of Nitrogen as Ammonia and as Nitric Acid, and of Chlorine in the Rain-water collected at Rothamsted. NORMAN H. J. MILLER (*J. Agric. Sci.*, 1905, 1, 280—303).—In addition to the whole of the analyses of the monthly samples of rain-water collected at Rothamsted to August, 1905 (compare *Proc.*, 1902, 18, 88), a summary is given of results (yearly averages) obtained at about thirty different places situated both in tropical and non-tropical countries (compare Ingle, this vol., ii, 302; and Leather, following abstract).

As regards total nitrogen, whilst considerable variations which are difficult to explain occur in the case of places similarly situated, it would seem that great differences in climate are not necessarily coincident with any very material difference in the amounts of nitrogen brought down by the rain, which only vary between 3 and 5 lbs. per acre per annum in places so differently situated as Rothamsted (3.84), Manhattan (3.64), Calcutta (2.99), Colombo (4.93), and British Guiana (2.99 lbs.). Whilst, however, in non-tropical countries most of the nitrogen (about 70 per cent.) is in the form of ammonia, in tropical rain the relation of nitric nitrogen is generally higher, and in some cases (Barbados and British Guiana) there is considerably more nitric nitrogen than nitrogen as ammonia.

Further analyses are very desirable, especially such as will throw

light on any differences in the composition of rain due to land and sea winds, both in tropical and non-tropical situations. N. H. J. M.

Composition of Indian Rain and Dew. JOHN W. LEATHER (*Mem. Dept. Agric. India. Chem. Ser.*, 1906, 1, No. 1, 11).—Determinations of nitrogen as ammonia and as nitrates and nitrites in samples of rain-water (generally two per month) collected at Dehra Dun from January to December, 1904, and at Cawnpore from May 1, 1904, to April 30, 1905 (compare this vol., ii, 302).

The dew collected in a large gauge (1/1000 acre) at Cawnpore from September 16, 1904, to March 15, 1905, amounted to 0.170 inch and contained nitrogen ammonia = 0.055, and nitric nitrogen = 0.056 lb. per acre, the amounts per million varying from 0.85 to 2.65 and 0.51 to 4.12 respectively. N. H. J. M.

Manurial Experiments with Calcium Cyanamide on Mineral and on Peaty Soils. Decomposition of Calcium Cyanamide in Different Soils. HJALMAR VON FEILITZEN (*Chem. Centr.*, 1906, i, 584—585; from *Verh. Ges. deut. Naturforsch. Aerzte*, 1904, ii, 157—159).—Satisfactory results were obtained with barley and wheat grown (in pots) in loamy and sandy soils, whilst in the case of oats and potatoes grown in peaty soil, calcium cyanamide had very little effect. N. H. J. M.

Calcium Cyanamide. E. WEIN (*Chem. Centr.*, 1906, i, 585; from *Verh. Ges. deut. Naturforsch. Aerzte*, 1904, ii, 162).—In loamy sand and in peaty soil containing 3 per cent. of calcium carbonate, calcium cyanamide gave, with barley, results similar to ammonium salts. As a manure for vegetables, calcium cyanamide was found to be equal to ammonium salts and in many cases equal to nitrates. The amount of lime in the soil is not very important. N. H. J. M.

Preservation of Farm-yard Manure. HEINRICH IMMENDORFF (*Chem. Centr.*, 1906, i, 584; from *Verh. Ges. deut. Naturforsch. Aerzte*, 1904, ii, 148—151).—Kainite and superphosphate gypsum at the rate of 1.5—2 kilos. per 1000 kilos. live weight of the animals had practically no effect on the loss of nitrogen. Sulphuric acid considerably diminished the loss, but its employment is not recommended. A larger amount of superphosphate gypsum (3 kilos.) gave better results, the loss of nitrogen being only 11.6 per cent. The best results were obtained with peat litter, loss of nitrogen being reduced to 7.3 per cent.

N. H. J. M.

Analytical Chemistry.

Simplified Measurement and Reduction of Gases. H. REBENSTORFF (*Chem. Zeit.*, 1906, 30, 486—487).—An apparatus for the rapid measurement of the volume of hydrogen evolved by the action of an

excess of acid on a known weight of metal. For the method of working, the original paper should be consulted. P. H.

Filter Tubes for Collection of Precipitates. SAMUEL L. PENFIELD and W. M. BRADLEY (*Amer. J. Sci.*, 1906, [iv], 21, 453—456).—The tubes consist of a piece of combustion tubing about 17 to 22 mm. diameter drawn out; a support of perforated platinum foil with a platinum wire soldered to its centre is inserted so that the wire drops into the narrowed portion of the tube; a layer of asbestos is then spread on the platinum. Instead of platinum a layer of powdered quartz may be used, and the asbestos is evenly spread on this by filling the tube with water, closing the lower end, suspending the asbestos in the water and then allowing it to flow. Several examples of experimental numbers are given as test of the accuracy of these filter tubes. L. M. J.

Application of the Pycnometric Method to the Determination of the Weight and Volume of Precipitates suspended in Liquids. HENRI GILLOT and A. GROSJEAN (*Chem. Centr.*, 1906, i, 867—868; from *Bull. Soc. chim. Belg.*, 19, 190—211).—If P = total weight of the mixture of precipitate and mother-liquor, D = sp. gr. of the mixture, V = total volume, p = weight of precipitate, p' = weight of filtrate, v = volume of precipitate, v' = volume of filtrate, d = sp. gr. of precipitate, and d' = sp. gr. of filtrate, then $p = (D - d')Vk$, in which k = weight of precipitate which corresponds with the difference of the sp. gr. of the mixture and the filtrate for a given volume v . k varies inversely with the sp. gr. of the precipitate and is readily determined for each substance: $k = p / (D - d')V$. Since $v = V - (P - p) / d'$,

$$d = p / V - (P - p) / d'.$$

The volume of precipitates in the condition in which they are formed is readily calculated from the results of pycnometric determinations by means of the above formulæ.

In the action of barium chloride on sodium sulphate, ammonia on aluminium sulphate, sodium hydroxide on copper sulphate and sulphuric acid on lead acetate, the absorption by the precipitate is practically nil, and it may be assumed that the composition of the filtrate which is readily withdrawn is the true composition of the mother liquor at the moment of formation of the precipitate. In the following table, the possible errors involved in the calculation for 10 grams of precipitate when the volume of the mixture is a litre and the weight of precipitate about 10 grams are given:

PbSO ₄	D6·29	± 0·018 c.c.	Mean of 4 expts.
BaSO ₄	D4·40	± 0·042 "	" " " 15 "
CuO, 2H ₂ O	D3·08 at 15°	± 0·126 "	" " " 4 "
Al ₂ O ₃ , 3H ₂ O	D2·46 at 15°	+ 0·184 "	" " " 4 "
CaC ₂ O ₄	—	+ 0·527 "	" " " 5 "

Cupric hydroxide is stable in very dilute solutions in presence of sugar.

In all the other reactions examined, except that of calcium chloride on ammonium oxalate, it was found that the formation of the precipi-

tate did not cause any absorption of the dissolved substance or of the solvent and that the value of k calculated from the sp. gr. of the filtrate corresponded with that calculated from the theoretical sp. gr.

Further details are given in the original paper and the effect of increase of D on the coefficient k is also discussed. E. W. W.

An Improved Extraction Cup. E. BRUCE WARREN (*Chem. News*, 1906, 92, 228).—Two designs of extraction cups are given, for which the original article should be consulted. The apparatus has been constructed for general extraction purposes and the novel feature is that the extraction takes place at the boiling temperature of the solvent, the cup being partly immersed in the solvent, whilst the condensed solvent from the reflux condenser falls into the cup.

L. DE K.

An Indicator for Strong Acids and Bases. HENRY J. H. FENTON (*Proc. Camb. Phil. Soc.*, 1906, 13, 298—299).—The condensation derivative of methylfurfuraldehyde of composition $C_{11}H_8O_4$, previously described by the author, has useful properties as an indicator (*Trans.*, 1903, 83, 187). Test papers, prepared from the aqueous-alcoholic solution, give a bright green with primary amines in acetic acid solution, and a bright blue with carbamide in hydrochloric acid. With alkalis, a fine violet-blue is obtained, and the variation of the colour intensity is a rough indication of the concentration of the hydroxyl ions. The colour is just visible in a 0.01*N* solution of potassium hydroxide or a 1.8*N* solution of ammonia. If the reagent is fused at about 120° with carbamide, a colourless base is obtained which gives blue colours with strong acids above decinormal concentration and with acetic acid at about 12—13 × *N*.

L. M. J.

Estimation of Moisture in Natural Solid Fuels. EUGENIO MANZELLA (*Gazzetta*, 1906, 36, i, 109—113).—The most satisfactory method yet proposed for estimating moisture in coals, &c., consists in heating the powdered coal in a current of dry hydrogen or carbon dioxide at 100°. This temperature is, however, not sufficiently high to remove completely the water from fuels which retain it tenaciously. A simpler method is to place a clock glass containing the powdered fuel in a Scheibler desiccator with phosphoric oxide above and underneath it, and then to evacuate the desiccator; all the moisture is removed in this way in at most twenty-four hours. The results obtained are very nearly the same as are given by heating the coal at 115° in a current of dry hydrogen.

T. H. P.

Detection of Iodides in the Dry Way. BERNHARD MERK (*Chem. Centr.*, 1906, i, 397; from *Pharm. Zeit.*, 50, 1022).—The substance is rubbed with 0.1 gram of potassium persulphate and 1 gram of starch, which will turn blue if iodides are present. L. DE K.

Back Reactions in Iodine Titrations. JOHN H. DAVIES and EDGAR P. PERMAN (*Chem. News*, 1906, 93, 225).—When titrating copper sulphate or potassium dichromate with potassium iodide and

thiosulphate, the decolorised liquid often turns blue again; permanganates or hypochlorites cause less trouble.

This back reaction may be prevented by using a sufficiency of potassium iodide. The authors recommend 1 gram of this salt in 10 c.c. of water for 25 c.c. of *N*/10 dichromate, and 2 grams in 20 c.c. of water for 1 gram of crystallised copper sulphate in 50 c.c. of water.

L. DE K.

Estimation of Dissolved Oxygen in Sea Water. WILLEM P. JORISSEN and WILHELM E. RINGER (*Chem. Centr.*, 1906, i, 275—276; from *Chem. Weekblad*, 2, 781—791).—A comparison of the processes of Bjerrum and of Romijn. In both methods (which are really modifications of Winkler's process), use is made of an alkaline solution containing manganous chloride, potassium iodide, and sodium hydroxide, but Romijn also adds sodium potassium tartrate to prevent the formation of a precipitate. The authors now state that this addition causes a slight deficiency in the amount of oxygen determined, at least when dealing with sea water, which contains large proportions of calcium and magnesium salts.

L. DE K.

Estimation of [Combined] Nitric Acid in Water. PAUL DRAWE (*Chem. Zeit.*, 1906, 30, 530—531).—One hundred c.c. of the sample are evaporated to dryness with addition of pure hydrochloric acid, and, after expelling the last traces of acid by repeated moistening with water and drying, the residue is dissolved and titrated with *N*/10 silver solution. From the result is deducted first the number of c.c. of silver required by the pre-existing chlorine, and also the number of c.c. of *N*/10 acid required for the neutralisation of any earthy or alkali carbonates.

The balance of *N*/10 silver is then calculated into nitric acid.

L. DE K.

Estimation of Water-soluble Phosphoric Acid and Total Phosphoric Acid in Superphosphates. KARL ROHM (*Chem. Zeit.*, 1906, 30, 542—543).—A series of experiments, fully tabulated, showing the importance of using a shaking apparatus when making an aqueous extract of a superphosphate, and also the advantage of a stirring apparatus when precipitating the phosphoric acid with the magnesium citrate mixture. The phosphate should be dissolved in nitro-hydrochloric acid, nitric acid, or mixed sulphuric and nitric acids, not in hydrochloric acid alone.

L. DE K.

Modified Bettendorf's Reagent. ANNIBALE FERRARO and ARTURO CAROBBIO (*Chem. Centr.*, 1906, i, 398; from *Boll. Chim. Farm.*, 44, 805—807).—A few centigrams of dry substance are heated in a test-tube with a few centigrams of metallic tin and about twelve drops of strong hydrochloric acid. In the presence of traces of arsenic, the liquid turns reddish-brown, and, finally, gives a more or less abundant black deposit. Antimony gives at once a black deposit, but leaves the supernatant liquid colourless.

If the substance is coloured, a little more tin should be used so as to reduce the colouring matter. L. DE K.

Detection of Boric Acid. GIUSEPPE VELARDI (*Gazzetta*, 1906, 36, i, 230—232).—The author suggests an improvement of the method of testing for various acids given by Castellana (*Abstr.*, 1905, ii, 420), which he carries out as follows. A short length of glass tubing is drawn out to a fine point at one end, and the mixture of substance and potassium ethyl sulphate introduced at the other end, which is then fused up. The tube is turned so that the substance falls into the sealed end, which is then heated, the vapours evolved being ignited. It is found, however, that a green flame is obtained with ammoniacal cuprous chloride, cupric chloride and carbonate, sodium chloride, ammonium chloride, sodium phosphate or chloral, as well as with a borate. The author finds that 0.0001 gram of sodium borate can be detected by means of turmeric paper, whilst Castellana's method is not sensitive to less than 0.0005 gram of borax. T. H. P.

Detection of Boric Acid. Reply to Velardi. VINCENZO CASTELLANA (*Gazzetta*, 1906, 36, i, 232—236. Compare preceding abstract).—The coloured flames obtained by Velardi (*loc. cit.*) with other substances than borates are caused by particles of the solid being carried along with the vapours owing to the shape of the tube used by this author. The sensitiveness of the reaction of boric acid with turmeric paper is disturbed by the presence of other substances. T. H. P.

Estimation of Boric Acid, alone and in the Presence of Phosphoric Acid. RODGER J. MANNING and WILLIAM R. LANG (*J. Soc. Chem. Ind.*, 1906, 25, 397—398).—This paper deals primarily with the separation of boric acid as the trimethyl ester and its subsequent gravimetric estimation as the barium salt. The boric acid, or one of its salts acidified with sulphuric acid, is distilled with about 350 c.c. of methylated spirit and the distillate received in a vessel containing concentrated barium chloride solution. The distillate is then exactly neutralised with $N/2$ sodium hydroxide solution and the resulting precipitate of barium borate, $Ba(BO_2)_2$, collected on a filter, washed with alcohol, dried at 110° , and weighed. An alternative method is to receive the distillate in water and titrate the boric acid in the usual way, after the addition of glycerol.

Where both borates and phosphates occur in a mixture, the latter is treated with $N/10$ sulphuric acid until acid to methyl-orange in order to liberate the phosphoric and boric acids. $N/5$ sodium hydroxide solution is then run in until the solution is neutral to this indicator. Glycerol is now added and the titration of the boric acid completed. W. P. S.

An Improved Form of the William Thomson Calorimeter. THOMAS GRAY (*J. Soc. Chem. Ind.*, 1906, 25, 409—411).—Some modifications have been introduced to render the original apparatus more durable and more convenient to handle. They consist in the substitution of thin perforated brass discs for the wire gauze baffles and the

replacement of the bulged glass combustion chamber by a straight, somewhat wider, glass tube. An arrangement for the electrical ignition of the coal is also made. The glass combustion tube is about 6.5 inches long by two inches in diameter and rests loosely-clamped on a perforated metal base; a brass tube for supplying the oxygen passes through a thick-walled rubber tube attached to the drawn-out upper end of the combustion chamber. Two upright brass tubes are fixed to the metal base and joined at the top by a vulcanite cross-piece provided with terminals. Through one of these tubes passes an insulated wire connected with a short insulated vertical rod inside the combustion chamber. A second rod, bent into the form of a ring to support the crucible, is in connection with the metallic base. The upper ends of these two rods are slightly higher than the top of the crucible and are connected by means of a thin platinum wire which can be made to glow by the passage of an electric current. The current may be obtained from storage cells or from the ordinary lighting mains. In the latter case a resistance must be used, and this may consist of a bottle containing sodium hydroxide solution in which are placed two spiral copper electrodes, one at the bottom of the bottle and the other towards the top. The wire attached to the upper electrode is capable of being moved up and down through the cork of the bottle so as to regulate the distance between the electrodes. This distance must be such that the platinum wire above the crucible just glows. The wire connecting with the lower electrode is surrounded by a glass tube reaching from the cork nearly to the bottom of the bottle, and the whole is conveniently fixed to a board provided with terminals, a circuit-making key, &c. Further adjustment of the resistance may be effected by altering the concentration of the sodium hydroxide solution.

W. P. S.

Electrical Conductivity of Sea Water. ERNST RUPPIN (*Zeit. anorg. Chem.*, 1906, **49**, 190—194).—As the measurement of the electrical conductivity is now employed as a rapid and convenient method for determining the amount of salt in sea water, the author has made a series of measurements with samples of varying strengths at different temperatures and gives a table of the specific conductivities, in reciprocal ohms, at 0°, 15°, and 25°, of waters containing from 5 to 40 per cent. of salt.

G. S.

Sodium Nitrate in Preserved Meat. AMBROISE ANDOUARD (*J. Pharm. Chim.*, 1906, [vi], **23**, 417—418).—The author analysed three samples of saltpetre used in preserving pork, and found that instead of consisting of sodium nitrate they contained 84.65, 96.76, and 98.03 per cent. of sodium arsenate and 13.28, 2.20, and 1.47 per cent. of sodium nitrate respectively.

T. A. H.

Estimation of Opalescent Silver Chloride Precipitates. ROGER C. WELLS (*Amer. Chem. J.*, 1906, **35**, 508—509. Compare this vol., ii, 252).—Reference is made to statements in the earlier paper regarding time effects in nephelometry, and it is now pointed out that

the time factor must be carefully regulated for intense opalescences, but is of much less importance in the case of weak opalescences.

E. G.

Use of the Nephelometer. THEODORE W. RICHARDS (*Amer. Chem. J.*, 1906, 35, 510—513).—Wells' paper (this vol., ii, 252) is criticised, and it is pointed out that the chief precaution required in nephelometric work, namely, that the unknown solutions to be estimated must be treated in exactly the same way as the standard solutions used for comparison, was not emphasised.

E. G.

Methods for Determining the Hydraulic Value of Volcanic Pozzuolana. EUGENIO MANZELLA (*Gazzetta*, 1906, 36, i, 113—123).—With reference to the method of determining the hydraulic value of pozzuolana by measuring the amount of lime absorbed from lime-water in a given time, the author finds that clay and arable soil also absorb lime in this way. The latter absorption is, however, soon at an end, whilst that effected by the pozzuolana gradually increases with the time. It is hence easy to distinguish hydraulically inert materials from true pozzuolana (compare Vicat, *Ann. Chim. Phys.*, 1826, 197, and Giorgis and Alvisi, *Abstr.*, 1900, ii, 348 and 545).

T. H. P.

Estimation of Cadmium. HENRI BAUBIGNY (*Compt. rend.*, 1906, 142, 792—793, 959—961. Compare this vol., ii, 307).—The metal should be in the state of sulphate and the liquid must contain at least 2 per cent. by volume of sulphuric acid. Organic acids do not interfere, but halogen acids should be absent. After heating to 90°, a current of hydrogen sulphide is passed until the liquid has cooled to 50°. In these circumstances, the precipitate is of a dense character, and may be collected and washed without difficulty. The filter and contents are now put into a Saxe crucible placed inside a porcelain crucible heated over a Wiessnegg burner. A moderate heat is applied until the paper has completely charred, and, after placing over the crucible an inverted perforated funnel, the temperature is raised to 500°, which suffices to burn the paper completely. The residual cadmium sulphide is now redissolved in hydrochloric acid and evaporated with sulphuric acid and, finally, heated to about 500° to convert it into sulphate, which is then weighed.

In presence of halogen acids, the cadmium sulphide cannot be incinerated with the filter. In this case it must be washed off the filter into a dish; the clear supernatant liquid is, to prevent any loss, passed again through the filter. After burning the filter in the manner described, the whole of the precipitate is converted into sulphate.

L. DE K.

Detection and Estimation of Very Small Quantities of Lead in Water. BERNHARD KÜHN (*Chem. Centr.*, 1906, i, 1563—1564; from *Arb. Kais. Ges.-A*, 23, 389—420).—The errors caused by the incomplete precipitation of lead sulphate and by the burning of the filter paper, render the gravimetric estimation of small quantities of lead less trustworthy than the volumetric. A freshly-prepared mixture of

25 c.c. of glacial acetic acid with 500 c.c. of a solution of sodium sulphide containing 8 grams in 500 of water is added to 4—5 litres of the water in which the lead is to be estimated. In order to filter the colloidal precipitate of lead sulphide which is formed, 100 grams of sodium nitrate are added, and the mixture shaken with 2 grams of short fibres of pure asbestos; the nitrate causes the precipitate to form a coherent mass, which attaches itself completely to the surface of the asbestos. The fibres are then removed from the liquid by filtration through an asbestos filter, and the lead sulphide oxidised on the filter by means of hydrogen peroxide to which a small quantity of nitric acid has been added. The lead sulphate is dissolved in a solution of sodium acetate and the lead then estimated by Diehl and Topf's method (*Abstr.*, 1880, 752). The lead dioxide obtained by adding bromine water to the solution of the sulphate is treated with a solution of potassium iodide and sodium acetate acidified with acetic acid. The liberated iodine is dissolved by an excess of sodium thiosulphate solution, and the excess then titrated with centinormal iodine solution. 0.1 mg. of lead in a litre of water may be estimated in this way without evaporating. Frerich's method (*Apoth. Zeit.*, 17, 884) of removing the lead by means of cotton wool cannot be used for the estimation of lead in potable water, since the adsorptive power of different samples varies, and the metal is not always completely separated.

E. W. W.

Demonstration of the Amount of Clay in Soils. ADOLPH EMMERLING and F. SIEDEN (*Chem. Centr.*, 1906, i, 584; from *Verh. Ges. deut. Naturforsch. Aerzte*, 1904, ii, 155—157).—The soil (30 grams) is shaken with water and dyed, according to the amount of clay, with a measured amount of a solution of malachite-green. In the case of marls, the calcium carbonate is first removed by treatment with hydrochloric acid and subsequent decantation. Humus soils must first be moistened with 30 c.c. of a saturated solution of potassium dichromate and heated on a water-bath with 10 c.c. of strong sulphuric acid; in the case of peaty soils, this operation must be repeated. The soil is then washed until nearly free from acid. The clay and sand are then generally distinct.

N. H. J. M.

Estimation of Manganese in Cast Iron (Ferromanganese, Spiegeleisen). FRANZ KIETREIBER (*Chem. Centr.*, 1906, i, 400; from *Oesterr. Chem. Zeit.*, 8, 565—566).—Two grams of the sample are dissolved in 20 c.c. of hydrochloric acid, 150 c.c. of water are added, and the solution is boiled with addition of two grams of potassium chlorate. Three c.c. of sulphuric acid are added and the whole evaporated until sulphuric fumes appear. The residue is rinsed into a litre flask, a sufficiency of zinc oxide is added, and the whole diluted up to the mark. Two hundred and fifty c.c. of the filtrate are then largely diluted, mixed with 20 c.c. of 10 per cent. zinc sulphate solution, and, after adding 2 drops of dilute nitric acid, titrated at the boiling temperature with permanganate. Another 250 c.c. may be acidified with sulphuric acid and titrated with permanganate in the cold.

Schneider's process may be applied as a check. 0.5 gram of the

sample is ignited for an hour in a muffle with 0.5 gram of sodium carbonate and 2 grams of magnesium carbonate. The mass is dissolved in 25 c.c. of dilute hydrochloric acid (1:2), mixed with 25 c.c. of dilute sulphuric acid, neutralised with zinc oxide, and diluted to one litre. Five hundred c.c. of the filtrate are then titrated with permanganate according to Volhard's method. L. DE K.

Detection and Estimation of Minute Quantities of Iron. ANTOINE MOUNEYRAT (*Compt. rend.*, 1906, 142, 1049—1051).—When a very dilute solution of a salt of iron is made alkaline with excess of ammonia and a current of hydrogen sulphide is then passed through it, a deep green coloration is produced if not less than one part of iron per million is present. The production of the colour is inhibited by the presence of the common mineral acids or their sodium salts, but is not affected by organic acids, glycerol, sucrose, mannitol, and similar substances. In presence of albumin, the reaction becomes more delicate. The green product does not dialyse.

Mercury, lead, silver, chromium, nickel, cobalt, copper, and the alkaline earths give no coloration when similarly treated. Copper, however, interferes with the delicacy of the reaction, and should be removed by precipitation with hydrogen sulphide before applying it. The intensity of the colour produced is proportional to the amount of iron present between the limits 1 per 1000 and 1 per million, and within these limits the reaction may be used for the colorimetric estimation of iron. T. A. H.

Analysis of Iron Ores and Slags. V. MACRÌ (*Chem. Centr.*, 1906, i, 395; from *Mon. Sci.*, [iv], 20, 18).—The solution freed from silica is divided into three portions. In the first, iron, aluminium, and manganese are precipitated by adding ammonium chloride, ammonia, and bromine; in the second portion, the iron is titrated with stannous chloride, and in the third, the manganese is titrated according to Volhard's method after removing iron and aluminium with zinc oxide. L. DE K.

New Test for Nickel. C. REICHARD (*Chem. Zeit.*, 1906, 30, 556—557).—If a trace of nickel sulphate (chloride or nitrate) is intimately mixed with a little methylamine hydrochloride and heated in a deep porcelain dish, the mass gradually turns a deep blue, which colour, however, again fades on cooling. Cobalt salts which give a similar colour retain, however, the blue colour on cooling. The test may be repeated time after time until the reagent has volatilised. The dirty-yellow residue may then, if desired, be mixed with a fresh portion of the reagent and again heated. The test seems characteristic of nickel. L. DE K.

Estimation of Chromium and Manganese. A. KLEINE (*Chem. Centr.*, 1906, i, 160; from *Stahl. u. Eisen*, 25, 1305—1306).—The sample of iron or steel is dissolved in hydrochloric acid, oxidised with nitric acid, evaporated to syrupy consistence, and freed from iron by treatment with ether. The residue is then boiled with dilute

sulphuric acid and ammonium persulphate, and the chromic acid in the filtrate and, finally, the manganic dioxide in the residue are titrated as usual.

L. DE K.

Separation of Tungsten from Tin. HENRY ANGENOT (*Zeit. angew. Chem.*, 1906, 19, 956).—A controversy with Donath (this vol., ii, 309). Donath's process is not quite so accurate as that of the author, as he disregards the small quantity of tungsten dioxide which remains in the filtrate.

L. DE K.

Colorimetric Estimation of Small Amounts of Gold. RALPH N. MAXSON (*Zeit. anorg. Chem.*, 1906, 49, 172—177).—It is shown that small amounts of gold can be determined accurately by conversion into the red colloidal form and comparison with standard solutions of the same modification in a colorimeter. The reduction is effected most satisfactorily by the action of an aqueous solution of acetylene on the chloride. If the solutions are kept in glass vessels which have been steamed, and care is taken to prevent access of electrolytes, the colour is retained unimpaired for a considerable time. Tables illustrating the accuracy of the method, and showing the limits of dilution within which it can be employed, are given in the paper.

G. S.

Use of a Layer of Copper Oxide or Copper Oxide and Asbestos 5 cm. in Length, instead of the Usual Long Layer in Elementary Organic Analysis. J. MAREK (*J. pr. Chem.*, 1906, [ii], 73, 359—373. Compare Dennstedt, *Abstr.*, 1903, ii, 103; 1905, ii, 202).—The author describes a modification of Dennstedt's method of elementary organic analysis, in which a roll of copper gauze 4—5 cm. in length, which has been oxidised and heated to redness, is used instead of the layer of platinised quartz or rolled sheet platinum. If the roll of copper gauze is packed into the tube with asbestos so that the gas must pass through the roll, it is sufficient to pass the current of oxygen at the rate of 30—35 c.c. per minute. The tube used is 30—45 cm. in length and 20 mm. in diameter, and is drawn to a point at the end to which the calcium chloride tube is attached. The pointed end is filled with filigree silver, or, if the substance contains nitrogen, sulphur, or a halogen, with a layer of lead peroxide, between two short plugs of filigree silver, 8—10 cm. in length. The lead peroxide must be heated during the combustion in an air-bath at 180—200°. An arrangement for separating the porcelain boat from Dennstedt's inner glass tube, to allow of the oxidation of deposited carbon, and a simple form of combustion oven are described. In the analysis of volatile substances such as carbon disulphide, a modified form of Dimroth and Wislicenus' apparatus (*Abstr.*, 1905, i, 422) is used.

In the examples of analyses quoted, the percentages of carbon and hydrogen found agree closely with those calculated.

G. Y.

Combustion of Halogen Compounds in Presence of Copper Oxide. CHARLES J. ROBINSON (*Amer. Chem. J.*, 1906, 35, 531—533).—The following method is described for the combustion of halogen

compounds. A hollow cylinder, about 6 or 7 cm. long, and of such a diameter that it will just fit the combustion tube, is made of heavy copper wire gauze and is filled with pure lead chromate. This cylinder is placed just in front of the boat in a combustion tube filled in the usual way with copper oxide. The part of the tube containing the cylinder must be well heated before the substance begins to decompose. Analyses are quoted which indicate the accuracy of the method.

The method has also been applied to the estimation of nitrogen in halogen compounds. The cylinder of lead chromate is employed as in the previous case and the substance is mixed with lead chromate.

E. G.

Formation of Nitrogen Trioxide. New Test for Alcohol. JULIUS KÓSSA (*Chem. Centr.*, 1906, i, 213; from *Pharm. Centr.-Halle*, 1905, 46, 893—895).—If 90 per cent. ethyl alcohol is carefully poured on to an equal amount of 50 per cent. nitric acid so that two layers are formed, a white, cloudy layer appears at the surface of contact after a few minutes, and soon afterwards a green or bluish-green ring is observed on the lower side of this. The green layer sinks gradually, effervescence takes place, and acetaldehyde is formed. At 0°, the coloured layer is blue and no effervescence is observed. If excess of nitric acid is used and the mixture cooled after shaking, a grass-green liquid is first formed, the colour of which on cooling to 0° changes to a deep blue.

The observed behaviour is suggested as a sensitive test for ethyl alcohol (1 drop alcohol, 20 drops 50 per cent. nitric acid). Acetaldehyde, ethyl ether, acetone, and chloroform do not give the reaction.

H. M. D.

Low Temperatures and Chemical Analysis [Addendum]. ARSÈNE D'ARSONVAL and FRÉD. BORDAS (*Compt. rend.*, 1906, 142, 1179. Compare *ibid.*, 1058).—In the distillation of syrupy liquids containing a very small amount of alcohol, the authors employ carbon cooled in liquid air according to Dewar's method to obtain a more perfect vacuum.

M. A. W.

The Röse-Herzfeld and Sulphuric Acid Methods for the Estimation of the Higher Alcohols. VICTOR H. VELEY (*J. Soc. Chem. Ind.*, 1906, 25, 398—401).—The author considers that the Röse-Herzfeld method is untrustworthy, and that the sulphuric acid method is still more untrustworthy. Whilst the former may give fairly accurate results if all the necessary, but tedious, precautions are adopted, the disadvantage of the method lies in the fact that the increase in the volume of the chloroform due to the higher alcohols is extremely small. The choice of a standard alcohol is one of the chief defects of the sulphuric acid method, the manner of heating and the difficulty of comparing the colorations produced also introducing inaccuracies.

W. P. S.

Reaction of Cholesterol with δ -Methylfurfuraldehyde. CARL NEUBERG (*Zeit. physiol. Chem.*, 1906, 47, 335).—The test described by

the author and Dora Rauchwerger (Abstr., 1905, ii, 122) does not, as stated previously, serve to distinguish cholesterol from phytosterol—both substances give the same reaction. W. D. H.

Osazone Test for Dextrose and Lævulose as Influenced by Dilution and by the Presence of other Sugars. HENRY C. SHERMAN and R. H. WILLIAMS (*J. Amer. Chem. Soc.*, 1906, 28, 629—632).—Mulliken (*Identification of Pure Organic Compounds*) has devised a method for identifying the sugars by means of the difference in the time required for the formation of osazones. The results which he obtained with dextrose, lævulose, sucrose, maltose, and lactose have now been confirmed, and determinations have also been made of the time required for the precipitation of the osazones of dextrose and lævulose in more dilute solutions, and of the influence of other sugars on the formation of these osazones.

It has been found that when equal volumes of dextrose solutions are treated with fixed amounts of phenylhydrazine hydrochloride and sodium acetate, the time required for the precipitation of the osazone varies with the amount of dextrose present, and is nearly constant for any given dilution. In the case of lævulose, there is a similar variation with the concentration, but the solutions yield a precipitate of the osazone in about one-third of the time required by the same quantity of dextrose. From invert-sugar solutions, the osazone separates almost as rapidly as from lævulose solutions of the same concentration. The precipitation of the osazone from solutions containing only about 0.1 per cent. of dextrose is hastened considerably by the presence of 1 per cent. of sucrose, slightly by 5 per cent. of raffinose, and is retarded by the presence of maltose or lactose. Sucrose and maltose cause similar variations in the rate of precipitation of the osazone from lævulose solutions, but the effect is less noticeable than in the case of dextrose, as the rate of osazone formation is much more rapid. E. G.

Analysis of Sugar Mixtures. CHARLES A. BROWNE, jun. (*J. Amer. Chem. Soc.*, 1906, 28, 439—453).—The author shows that the reducing power of a sugar will remain constant for any concentration, provided the same amount of copper in solution is maintained throughout the experiment. In other words, the reducing power diminishes, not on account of the increased concentration of the sugar, but because less copper remains in the solution to be acted on.

The difference in reducing power of the various sugars on Fehling's solution can be expressed simply as follows: if a definite weight d of a sugar D and a definite weight l of a sugar L reduce the same weight of copper, the ratio $d:l$ will be a fixed quantity, that is, the various reducing sugars bear a constant ratio to one another for the same weight of reduced copper. For dextrose : lævulose, this ratio has the value 0.915; for dextrose : galactose, 0.898; for dextrose : xylose, 0.983; and for dextrose : arabinose, 1.032. By means of these dextrose ratios, determinations can be made of any reducing sugar by Allihn's method, the weight of dextrose given by the table divided by the proper dextrose ratio being the weight of sugar sought. The author has been unable to verify the statement that, in a mixture of

reducing sugars, the reducing powers of the individual sugars are somewhat modified by the other sugars present.

In a mixture containing x per cent. of a given reducing sugar A , having the dextrose ratio a , and y per cent. of another reducing sugar B , having the dextrose ratio b , the percentage, R , of total reducing sugars calculated as dextrose is given by $R = ax + by \dots (1)$.

If 26.048 grams of the mixture are dissolved to give 100 c.c. of solution and the polarisation read in a 200 mm. tube in a Ventzke-Scheibler instrument, the polarisation of any sugar is equal to its percentage multiplied by a polarisation factor, found by dividing the specific rotation of the sugar by that of sucrose ($+66.5^\circ$). Thus, if α and β are the respective polarisation factors of the sugars A and B , and P the polarisation of the mixture, $P = \alpha x + \beta y \dots (2)$.

From (1) and (2) we obtain: $x = (bP - \beta R) / (ab - a\beta)$ and $y = (R - ax) / b$. This method was found to give good results.

With a mixture of dextrose, lævulose, and sucrose, the polarisation is expressed by P (at 20°) $= S + 0.793D - 1.356L$, where S , D , and L are the percentages of the three sugars. If S be determined by Clerget's method, we have $L = (0.793R + S - P) / 2.08$ and $D = R - 0.915L$, R being the percentage of total reducing sugars calculated as dextrose. This method involves the following two sources of error: (1) The reducing action of sucrose, which is proportional to the concentration of sucrose and to the amount of copper left unreduced. The following correction of this error gives concordant results: the number of grams of sucrose in the 25 c.c. of solution to be analysed by Allihn's method is divided by the number of mg. of dextrose found plus 40; the quotient gives the required correction in grams which is to be subtracted from the found amount of reducing sugar. (2) The change in rotation of lævulose in the acid solution used in determining the sucrose by Clerget's method. If 10 c.c. of fuming hydrochloric acid (sp. gr. 1.18) are used per 100 c.c. of sugar solution, the correction to be subtracted from the percentage of sucrose obtained by Clerget's method is 0.036 for each 1 per cent. of lævulose. T. H. P.

Estimation of Sugar in Urine. RICHARD LEVY (*Chem. Centr.*, 1906, i, 1513; from *Münch. med. Woch.*, 53, 212—214).—Riegler's permanganate method, Pavy's method, and the polarisation method were compared. The two latter give correct and nearly identical results. Riegler's method is not so accurate. W. D. H.

Estimation of Sucrose, Reducing Sugars, and [Added] Starch in Chocolates. LUCIEN ROBIN (*Ann. Chim. anal.*, 1906, 11, 171—175).—12.5 grams of rasped chocolate are triturated repeatedly with water in a glass mortar, using in all 115 c.c., and to the mixture is added 5 c.c. of basic lead acetate. The whole is then brought on a filter and, after collecting the filtrate, the residue is well washed and kept for the starch determination. The main filtrate is then subjected to polarimetric and chemical treatment as usual, which gives the sugar in its various forms.

The insoluble matter is boiled with a mixture of 80 c.c. of water and 10 c.c. of hydrochloric acid, and the resulting dextrose is

estimated with the usual precautions. As cocoa contains natural starch it is unnecessary to go through this process, unless a microscopic test has revealed the presence of added starches. If the difference between 100 and the percentage of total sugars is called cocoa, the natural starch may be assumed to be $\text{cocoa} \times 0.097$; any excess found is, therefore, added starch. L. DE K.

Detection of Sugar in Mace and Cinnamon. EDUARD SPAETH (*Zeit. Nahr. Genussm.*, 1906, 11, 447—450).—Ten grams of the sample, previously treated with light petroleum to remove the fat, are shaken with chloroform, the mixture allowed to settle, and the chloroform decanted. The last few c.c. with the sediment are evaporated, the residue is dissolved in warm water and transferred to a 50 c.c. flask. After the addition of 2.5 c.c. of lead acetate solution and 2.5 c.c. of aluminium hydroxide emulsion, the mixture is diluted with water to the mark, filtered, and the filtrate examined in the polariscope. Pure samples of mace and cinnamon do not contain sugar which polarises light, and any added sugar will therefore be detected by the above process. The amount of sugar occurring in mace, and not indicated by the polariscope, is about 2 per cent. W. P. S.

Estimation of Insoluble Amyloses in Starches. JULES WOLFF (*Ann. Chim. anal.*, 1906, 11, 166—167. Compare Abstr., 1905, ii, 866).—The total amount of amyloses is obtained by heating 2.5 grams of the starch with 50 c.c. of water at $140\text{--}150^\circ$ for thirty minutes. The solution is then allowed to cool to 65° , and at once treated as usual with 10 c.c. of infusion of malt. The liquid is diluted to 200 c.c., and 100 c.c. of the filtrate are fully inverted as usual by means of 1 c.c. of sulphuric acid in an autoclave, and the resulting dextrose is determined as usual, allowance being made for the dextrose contained in the malt. Two further experiments are then made in a similar manner, but with solutions which have been exposed to temperatures of 100° and 65° respectively. The difference shows the less readily convertible amyloses. L. DE K.

Formaldehyde and its Reactions. JULIUS SCHUCH (*Chem. Centr.*, 1906, i, 501—502; from *Zeit. landw. Versuchswes. Oesterr.*, 8, 1058—1060).—The author tested several methods as to their suitability for the detection of formaldehyde in wines and in presence of acetaldehyde. The best process is that given by Arnold and Mentzel. Three hundred c.c. of wine are distilled until 10 c.c. have passed over; 5 c.c. are shaken with 1.5 c.c. of a solution of phenylhydrazine hydrochloride (1:50) and four drops of ferric chloride and twelve drops of sulphuric acid are added. In the presence of formaldehyde, a rose or dark red coloration is formed. L. DE K.

Phenanthrene Reaction. II. C. REICHARD (*Chem. Centr.*, 1906, i, 1576; from *Pharm. Centr.-Halle*, 47, 309—311. Compare *Pharm. Centr.-Halle*, 46, 813).—When phenanthraquinone is dissolved in an excess of a warm concentrated solution of sodium hydrogen sulphite, a colourless, crystalline mass separates on cooling. Two-thirds of

the solid deposit again becomes liquid, however, after remaining for some weeks, and a reddish to reddish-brown ring is formed at the edge of the crystalline mass; this portion soon changes to grey and decreases in volume until the whole has become a homogeneous grey mass; the supernatant liquid is bright green. E. W. W.

Detection of Acetoacetic Acid in Urine. OTTO MAYER (*Chem. Centr.*, 1906, i, 406; from *Pharm. Zeit.*, 50, 1001—1002).—A few c.c. of a mixture of 5 c.c. ferric chloride solution and 95 c.c. of brine are introduced into a test-tube, and an equal volume of urine is gently poured on to it. In the presence of acetoacetic acid, a more or less intense claret-red ring will be observed. If the sample is diluted previously to such an extent that a red colour is only just visible, the liquid may be assumed to contain 0.01 per cent. of the acid, and the amount in the undiluted sample may thus be calculated.

The test should be repeated after boiling the urine for five minutes, and it should then be negative. Salicylic acid, if present, may be extracted by means of chloroform. Diacetoacetic acid may be extracted from the acidified urine with ether. L. DE K.

[**Estimation of**] **Cholic Acid occurring in Human Fæces.** FELIX VON OEFELE (*Zeit. öffentl. Chem.*, 1906, 12, 189—190).—For the estimation of cholic acid in fæces, the author makes use of the fact that, whilst cholic acid in the amorphous condition is soluble in ether, treatment with water and alcohol converts it into a crystalline form which is insoluble in this solvent and permits of the separation of other substances extracted by ether. From the results obtained, it appears that the acids occurring in normal fæces, and considered previously as fatty acids, are cholic acids. W. P. S.

Estimation of Uric Acid. GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1906, [vi], 23, 516—517).—About 125 c.c. of the urine in which it is desired to estimate the uric acid are treated with 1 gram of dry sodium carbonate and the precipitated phosphates are filtered off. To 100 c.c. of the filtrate are added 25 c.c. of 50 per cent. ammonium nitrate solution and 5 c.c. of ammonia. At the end of twenty-four hours, the precipitate of ammonium urate is collected on a filter, washed with the ammonium nitrate solution, to which is added 1 per cent. of ammonia, and then transferred from the filter to a flask by the aid of a jet of water. Forty c.c. of dilute sulphuric acid (1:2) are added, the solution is heated to a temperature of 50°, and titrated with a potassium permanganate solution containing 1.5 grams per litre. The number of c.c. of permanganate solution required multiplied by 0.00356 gives the percentage of uric acid in the urine. In case the urine contains any urates already deposited, it should be heated until the deposit is dissolved before commencing the estimation. The method may be applied directly to urines containing albumin.

W. P. S.

Experiments with Röhrig's Modification of the Gottlieb-Röse Apparatus. P. GORDAN (*Milchw. Zentr.*, 1906, 2, 224—227).—Estimations of fat in eight samples of cream, twelve samples of milk,

and eight samples of skimmed milk show that trustworthy results may be obtained by the apparatus (Abstr., 1905, ii, 490), the figures being in close agreement with those yielded by Gerber's method. The proportion of ether to light petroleum used is of importance and should not differ greatly from that originally recommended. If a mixture of 10 c.c. of ether with 40 c.c. of light petroleum is employed, the results obtained will be much too low, and as the amount of non-fatty substances extracted by the solvent is quite small, there is no occasion to alter the composition of the solvent (compare Abstr., 1905, ii, 773). W. P. S.

The Sesamé Oil Reaction. PAUL SOLTSIEN (*Chem. Rev. Fett. Harz. Ind.*, 1906, 13, 138).—Sesamé oil which has been extracted repeatedly with hydrochloric acid no longer gives the characteristic reaction with furfuraldehyde, but the coloration obtained with stannous chloride is as intense as in the case of the unextracted oil. Hence these reactions must be due to two different constituents of the oil. W. P. S.

Estimation of Fat in Cocoa. AAGE KIRSCHNER (*Zeit. Nahr. Genussm.*, 1906, 11, 450—451).—The following application of Gottlieb's process to the estimation of fat in cocoa is described. About 1.5 grams of the cocoa are weighed out into a narrow graduated cylinder of 75 or 100 c.c. capacity, 20 c.c. of 50 per cent. alcohol are added, the cylinder is shaken to bring the alcohol into contact with the cocoa, and the mixture then shaken for fifteen minutes after the introduction of exactly 25 c.c. of ether. Twenty-five c.c. of light petroleum are next added and mixed by cautiously inverting the cylinder a few times. Care must be taken to avoid the formation of a troublesome emulsion. The mixture is then allowed to separate for one hour, when 45 c.c. of the ethereal layer are drawn off, evaporated, and the residue of fat is weighed. The presence of the cocoa prevents the total volume of the ethereal layer being read off directly, but the volume may be ascertained by making an exactly similar mixture without the cocoa. To the volume thus found is added the weight of the fat, 1 c.c. being added for each gram. The amount of fat in the cocoa is then calculated. W. P. S.

The Detection of Beef Fat in Lard. HARRY DUNLOP (*J. Soc. Chem. Ind.*, 1906, 25, 458—461).—A considerable number of results are given of analytical data obtained in the examination of fats rendered from different parts of the bodies of pigs, particular attention being paid to the appearance or shape of the crystals yielded by ethereal solutions of the fats. The author concludes that "plumose" groups of crystals are no proof of the presence of beef stearin unless the form of the individual crystals be observed, and that lard stearin cannot be eliminated from beef stearin by recrystallisation from ether, the latter being the more soluble of the two. As the weight of the ether-washed deposit (Stock's method) from genuine lard varies from 0.005 to 0.2 gram, it is dangerous to draw conclusions from such a test. Owing to the fact that the lard obtained from pigs fed on cotton-seed meal gives a coloration with Halphen's reagent, the conclusion that a

lard containing cotton oil probably also contains beef fat as a "stiffening" agent cannot be trusted. W. P. S.

Test for "Saccharin" and a Simple Method of Distinguishing Coumarin from Vanillin. JOSEPH H. KASTLE (*Chem. Centr.*, 1906, i, 1575—1576; from *Public Health and Marine-Hospital Service U.S. Hygienic Lab. Bulletin* No. 26, 31—35).—When small quantities of "saccharin" are heated with a small quantity of a mixture of 5 c.c. phenol with 3 c.c. of concentrated sulphuric acid for five minutes at 160—170°, the solution obtained by dissolving the product in a small quantity of water and adding a solution of sodium hydroxide becomes purple-red or rose-red according to the quantity of "saccharin" present. An excess of the reagent should be avoided. 0.025 mg. of "saccharin" can be detected, but in this case only a very small quantity of reagent should be used, and the temperature kept at 145—160°. Salicylic and benzoic acids form only a faintly yellow solution when heated with the reagent after the addition of sodium hydroxide, and the presence of these acids does not interfere with the sensitiveness of the test. Coumarin and ethyl *p*-sulphobenzoate do not give the reaction. When extremely small quantities of vanillin are mixed with the reagent, it becomes yellow and then red, and when heated at 160—170° for some minutes the mass turns blood-red and finally black; the solution in water becomes dark red on the addition of a few drops of a 2-*n* sodium hydroxide solution. Vanillin is attacked in the cold, but "saccharin" does not react even at 100°.

Coumarin does not give a coloration when heated with phenol and sulphuric acid at 160—170°, but other phenols give characteristic colour reactions both with "saccharin" and vanillin. When the phenol in the above test for "saccharin" is replaced by the following phenols, the colours mentioned first in each case are formed, but when vanillin is used and the temperature kept at 100°, the second coloration is produced: catechol, green; dark grey to green. Quinol, dark reddish-brown with blue fluorescence; dark reddish-brown. Resorcinol, salmon colour; red with faint green fluorescence. Tricresol, purplish-red; deep purplish-red. Phloroglucinol, wine-red; yellow. Thymol, bright blue; bright red. By the action of coumarin and sulphuric acid at 100° on the above phenols, colourless (tricresols) to orange-yellow (phloroglucinol) compounds are formed. E. W. W.

New Reaction of Terpeneol. C. REICHARD (*Chem. Centr.*, 1906, i, 403; from *Pharm. Centr.-Halle*, 46, 971—972).—If a few drops of a strong solution of potassium thiocyanate are heated until the formation of a crust and a drop of terpeneol is added, the mass on being moistened with a drop of sulphuric acid turns brownish-red, sometimes blood-red or brown, which colours finally pass into yellow. Terpene hydrate and oil of turpentine give the same reaction.

A mixture of terpeneol, terpene hydrate, or oil of turpentine mixed with solid sodium metasilicate and a drop of sulphuric acid, turns a fine blood-red. L. DE K.

Copaiba Balsam. FRANZ UTZ (*Chem. Centr.*, 1906, i, 709; from *Apoth. Zeit.*, 1906, 21, 72—73).—The refractive indices at 15° of a number of balsams from various sources have been determined and, although they vary within wide limits, a determination of this constant enables the presence of fatty oils or turpentine oil, but not of gurjun balsam, to be detected in copaiba balsam. P. H.

Tannins. HERMANN THOMS (*Chem. Centr.*, 1906, i, 291—292; from *Ber. deut. pharm. Ges.*, 15, 303—347).—A very pure tannin may be obtained by agitating a 25 per cent. aqueous solution with ether, which causes the formation of three layers. The bottom layer is then withdrawn and evaporated in a vacuum over sulphuric acid. Pure tannin is not precipitated by ammonium sulphate; the tannins from extract of belladonna are, however, precipitated.

Glückmann's process of estimating tannin by means of formaldehyde is untrustworthy in presence of gallic acid, phloroglucinol, or pyrogallol, as these substances also readily react with formaldehyde. The investigation is being continued. L. DE K.

Precipitation of Tannins by Ammonium Salts. C. VIRCHOW (*Chem. Centr.*, 1906, i, 292; from *Ber. deut. pharm. Ges.*, 15, 348—352).—Tannins are as a rule not precipitable by ammonium sulphate, but under the influence of certain reagents, such as ethyl acetate, followed by exposure to a temperature of 140°, they suffer decomposition and become partly precipitable. The tannins of extract of belladonna are also precipitated; their true nature still needs to be investigated. L. DE K.

Estimation of Gallotannic Acid in Tanning Materials. A. MANEA (*Chem. Centr.*, 1906, i, 406; from *Bull. Soc. Sci. Bucharest*, 14, 471—474).—A mixture is prepared containing 840 c.c. of 10 per cent. solution of lead acetate and 60 c.c. of acetic acid; 54 c.c. of this are diluted with 600 c.c. of water and the tannin solution is added from a burette so long as a precipitate is formed. Gallic acid is not precipitated. The precipitate is at once collected and rapidly washed with warm water. One gram of pure lead tannate = 0.5563 gram of gallotannic acid. L. DE K.

Nessler's Reagent as a Test for Saponin. JEAN VAMVAKAS (*Ann. Chim. anal.*, 1906, 11, 161—163).—A process devised for the detection of saponin (infusion of soap-root) in effervescing drinks; it is not, however, applicable to wines and beers. One hundred c.c. of the beverage are well boiled, and when cold the liquid is made up to the original volume, and basic lead acetate is added until a white precipitate has formed. The precipitate is collected on a filter and washed and then suspended in water and decomposed by hydrogen sulphide.

In presence of saponin, the resulting filtrate forms a lather on shaking, and if, after boiling to expel the hydrogen sulphide, an aliquot portion is mixed with a few drops of Nessler solution, a yellow pre-

cipitate is at once formed which on boiling turns greenish-blue or greenish-black.

If to another portion tartaric acid is added, no reaction will be obtained even on boiling.

L. DE K.

Volumetric Estimation of Cyanates. ALEXANDER C. CUMMING and ORME MASSON (*Chem. News*, 1906, 93, 5—6, 17—18; from *Proc. Soc. Chem. Ind. Vict.*, 1905).—The strongly diluted solution, which generally also contains carbonates, is titrated with $N/10$ sulphuric acid, using methyl-orange, or preferably congo-red, as indicator, and taking the first end-point; this gives the carbon dioxide. Excess of acid is now added and the liquid is well boiled, cooled, and titrated back with $N/10$ sodium hydroxide; the acid consumed represents the cyanic acid. As a check, the ammonia formed from the cyanate may be estimated in the usual way by adding an excess of alkali and, after boiling, titrating with $N/10$ acid. It is, of course, taken for granted that no ammonia pre-exists in the solution.

If cyanides are also present, the hydrocyanic acid should be titrated with $N/10$ silver nitrate in the usual manner and the necessary correction applied to the carbonate. If it is desired to check the result by a gravimetric estimation, the carbonate may be precipitated with barium nitrate and the filtrate with silver nitrate. Any cyanide should be allowed for.

The process has been found to work well with commercial potassium cyanide, which usually contains cyanate, if only great care is bestowed on the cyanide titration.

L. DE K.

Action of Sodium Hypobromite on Carbamide and on Ammonium Salts. REMO CORRADI (*Chem. Centr.*, 1906, i, 1574—1575; from *Boll. Chim. Farm.*, 45, 181—185).—Dupré's azotometer is recommended for measuring the nitrogen evolved by the action of sodium hypobromite on carbamide. The hypobromite is contained in a flask with a wide opening by means of which the tube containing the liquid to be tested is introduced. The flask is connected with a bell jar graduated in $1/10$ c.c., which is filled with water and stands in a cylinder containing water. Experiments show that the quantity of nitrogen obtained is from 9.8 to 14.6 per cent. too low, and that the results may vary by 4.8 per cent., but that when a concentrated solution of sucrose is added, in accordance with Méhu's suggestion (*Abstr.*, 1880, 681), the deficit is reduced to 3.8—5.4 per cent. and the maximum variation does not amount to more than 1.6 per cent. The presence of other nitrogenous substances tends to compensate the error, but when sucrose, lead acetate, and sodium carbonate are added and the liquid filtered, the method gives results which are about 2.4 per cent. too low.

On an average only 94 per cent. of the theoretical quantity of nitrogen is obtained by the action of sodium hypobromite on ammonium salts.

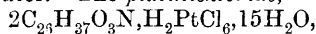
E. W. W.

Detection of Guanidine. D. ACKERMANN (*Zeit. physiol. Chem.*, 1906, 47, 366—367).—The usual method of detecting guanidine in the

decomposition products of proteid is to remove the arginine in the "arginine fraction" by picronic acid, and then precipitate with picric acid. Benzene sulphonic chloride is recommended in place of picric acid; the benzene sulphoguanidine so obtained is very insoluble, and can thus be easily separated, even if arginine is still present. It can be obtained as white crystals from an alkaline solution, and melts at 212°.

W. D. H.

Alkaloids of the Rhizome of *Veratrum album* and their Estimation. C. BREDEMANN (*Chem. Centr.*, 1906, i, 606—608; from *Apoth. Zeit.*, 1906, 21, 41—45 and 53—56).—The alkaloids may be estimated by shaking 12 grams of powdered material with 120 c.c. of a mixture of equal volumes of ether and chloroform, adding 10 c.c. of sodium hydroxide and frequently shaking the mixture during three hours. Water is now added until the powder clogs together and the ether-chloroform layer is run off, clarified with magnesium oxide and three or four drops of water, and 100 c.c. are filtered. The filtrate is extracted three times with water acidified with acetic acid and, after making the acid extract alkaline, it is shaken up three times with a mixture of ether and chloroform; after evaporating the solvents, the residue is dried at 100° and weighed. The percentage of alkaloids was found by this method to vary from 0.19928 to 0.93280. The pure alkaloids were obtained by macerating 5 kilos. of coarsely powdered material for several days with a mixture of two parts of ether and one part of chloroform in the presence of sufficient sodium hydroxide. After pouring off the solution and evaporating to the consistency of a thin syrup, the latter was repeatedly shaken with dilute acetic acid, the alkaloids being subsequently separated from this aqueous solution by Salzberger's metaphosphoric acid method (compare *Abstr.*, 1891, 230). *Jervine*, $C_{26}H_{37}O_3N \cdot 2H_2O$, forms white, needle-shaped prisms and melts at 241°; it is readily soluble in chloroform, fairly so in alcohol, very slightly in ether, and practically insoluble in benzene or light petroleum. The *sulphate* crystallises from absolute alcohol in smooth, four-sided prisms. The *hydrochloride*, $C_{26}H_{37}O_3N \cdot HCl \cdot 2H_2O$, separates from absolute alcohol in short, four-sided, highly refractive prisms. The *nitrate*, $C_{26}H_{37}O_3N \cdot HNO_3$, forms four-sided prisms. The *acetate* crystallises in smooth, four-sided, highly refractive prisms containing water of crystallisation; it is more soluble in water than the other salts. The *phosphate* forms very slender, colourless needles which are readily soluble in water. The *aurichloride*, $C_{26}H_{37}O_3N \cdot HAuCl_4$, prisms, very slightly soluble in water. The *platinichloride*,



pale orange-coloured, amorphous powder, very slightly soluble in water.

Rubijervine, $C_{26}H_{49}O_9N \cdot H_2O$, forms needle-shaped prisms, melts at 234°, and is fairly soluble in hot chloroform, less so in alcohol, and only slightly so in ether or light petroleum.

Pseudojervine, $C_{29}H_{43}O_7N$, is obtained from the sulphate in thin, six-sided plates which melt at 304°; it is readily soluble in chloroform, very slightly so in alcohol, and practically insoluble in ether, light petroleum, or benzene. The *sulphate* forms long prisms and is fairly soluble in water, whilst the *hydrochloride* is only slightly soluble.

Protoveratrine separates from absolute alcohol in colourless, four- or six-sided plates; it is fairly soluble in chloroform and hot absolute alcohol, slightly soluble in cold ether, and insoluble in water, benzene, or light petroleum. From the mother liquors of the protoveratrine, a small quantity of an *alkaloid* has been obtained which crystallises from absolute alcohol in spherical aggregates of needles and melts at 239—241°, but the amount was too small to admit of its identification. The paper contains in addition a detailed account of a number of colour and other reactions of these alkaloids. P. H.

Estimation of Caffeine in Raw Coffee. CARL WOLFF (*Zeit. öffentl. Chem.*, 1906, 12, 186—189).—Caffeine may be estimated in raw coffee by extracting the latter for nine hours with chloroform in a Soxhlet's apparatus, evaporating the extract, and estimating the nitrogen in the residue obtained. Experimental proof is given that chloroform does not extract any nitrogenous substance other than caffeine from coffee. From some cause, the method is not applicable to roasted coffee, the results obtained being much too low and duplicate estimations not agreeing with each other. W. P. S.

A Reaction of Theobromine. G. GÉRARD (*J. Pharm. Chim.*, 1906, [vi], 23, 476—477).—To a solution of 0.05 gram of theobromine in 3 c.c. of water and 6 c.c. of sodium hydroxide solution are added 1 c.c. of ammonia and 1 c.c. of 10 per cent. silver nitrate solution. A colourless, transparent mass is obtained which, if heated in a water-bath to a temperature of 60°, becomes liquid and solidifies on cooling to a clear jelly. It is possible to obtain a solid jelly with as little as 0.01 gram of theobromine per 10 c.c. of solution. Caffeine does not give a jelly when thus treated. W. P. S.

Colorimetric Estimation of Morphine. L. GEORGES and GASCARD (*J. Pharm. Chim.*, 1906, [vi], 23, 513—516).—The method proposed is based on the coloration produced by the addition of iodic acid to a solution containing morphine. Five, 10, or 20 c.c. of the solution to be examined are placed in a tube and 5 c.c. of a 5 per cent. iodic acid solution are added. In a similar tube an equal volume of standard morphine solution is mixed with 5 c.c. of the iodic acid solution. After the lapse of half a minute, the colorations in the two tubes are compared and the amount of morphine in the first tube thus ascertained. The standard morphine solution should contain 1.256 grams of morphine hydrochloride per litre; 1 c.c. of this solution will be equivalent to 0.001 gram of morphine. Ammonia may be added in addition to the iodic acid, but the colour then develops more slowly and no advantage is obtained. Owing to the gradual development of the colour when iodic acid alone is used, the reagent should be added to both tubes at as nearly as possible the same time. W. P. S.

Toxicological Investigation of Strychnine. MARUSSIA BAKUNIN and VINCENZO MAJONE (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1905, [iii], 11, 333—360).—Of the various methods given for the determination of strychnine in animal organs, that of Dragendorff (*Ermittelung von Giften*, 1895) gives the best results. When a liver containing

0.003 gram of strychnine was examined by this method, 0.0025 gram of the alkaloid was found.

The experiments of the authors show that rarely more than one-tenth of the strychnine administered to the organism can be afterwards traced. If the animal is killed twenty-four hours after the administration of a non-lethal dose of the poison, the latter is not found in the organs. Only in cases where an amount of strychnine greater than the toxic dose is given are notable quantities afterwards found, and here, as in other instances, the organ containing the largest amount is always the stomach; in the liver and spleen, only minimal proportions occur. The bladder, kidneys, and urine often give negative results. In one case, the urine of a live rabbit showed the presence of strychnine. In the urine of dogs, the alkaloid is always found in amount corresponding with about one-tenth, or rather more, of that administered; after seventy-two hours, the elimination in this way ceases.

The quantity of strychnine administered and the time elapsing between administration and death have a marked influence, especially with regard to the amounts found in the stomach and liver; the effect is small in the cases of the other organs, which never contain more than small quantities.

In all probability, strychnine undergoes in the organs profound changes, which prevent all but a small portion from being traced.

Under the ordinary conditions of burial, the dispersion of the strychnine is effected less by putrefaction than by the loss of liquid from the corpse aided by the action of rain water. T. H. P.

Colour Reaction of Formaldehyde with Proteids and its Relation to the Adamkiewicz Reaction. OTTO ROSENHEIM (*Biochem. J.*, 1906, 1, 233—240).—Formaldehyde gives rise to a characteristic colour reaction with proteids in the presence of sulphuric acid containing oxidising agents. The same reaction is produced by the interaction of diformaldehyde-peroxide-hydrate with proteids and pure sulphuric acid. This reaction is due to the formation of a proteid-aldehyde compound and its subsequent oxidation; the reaction depends on the presence of the tryptophan (indole) group in the proteid molecule. No reaction was obtained with gelatin (absence of indole group).

The colour obtained is identical, both to the naked eye and to the spectroscope, with that produced in the Adamkiewicz reaction and in Hopkins and Coles' glyoxylic reaction. The Adamkiewicz reaction is not only due to impurities in the acetic acid used, but also to the presence of oxidising agents (nitrous acid, ferric salts, &c.) in the sulphuric acid employed. The question is discussed how far the Adamkiewicz reaction is due to the presence or formation of formaldehyde in the acetic acid used, and Hopkins and Coles' view on the importance of glyoxylic acid is criticised. W. D. H.

General and Physical Chemistry.

Emissive Power and Temperature of Auer Mantles containing Different Quantities of Cerium. H. RUBENS (*Ann. Physik*, 1906, [iv], 20, 593—600).—The maximum temperature of the mantle in an ordinary Auer burner with chimney is probably not higher than 1550—1600°, and it may be shown that the emissive power of the mantle for the blue rays is very high. The temperature is lower in those mantles which contain a larger proportion (up to 5 per cent.) of cerium, since they are characterised by greater emissive power in the infra-red portion of the spectrum. J. C. P.

Index of Refraction of Substances dissolved in Non-aqueous Solvents. C. CHÉNEVEAU (*Compt. rend.*, 1906, 142, 1520—1522. Compare Abstr., 1904, ii, 641).—Experiments with solutions of the chlorides of lithium, calcium, copper, magnesium, and tin (stannous) in ethyl alcohol, lithium chloride in methyl alcohol, zinc chloride in ethyl ether, and ammonium chloride in glycerol show that the difference between the index of refraction of the solution and that of the pure solvent is proportional to the concentration of the dissolved substance. The constant of proportionality has, moreover, practically the same value as for aqueous solutions of the same substances. Slight deviations from these simple relationships have been traced to small quantities of water in the dissolved substance or in the solvent. When the dissolved substance reacts chemically with the solvent, no such simple relationships are observable. H. M. D.

Absorption Spectrum of Ozone. ERICH LADENBURG and ERICH LEHMANN (*Chem. Centr.*, 1906, i, 1727—1728; from *Ber. Deut. phys. Ges.*, 4, 125—135).—By the evaporation of liquid ozone, a gas containing a high percentage of ozone is obtained; this gas is prone to explode. The absorption spectra of liquid and gaseous ozone have been examined photographically and thermoelectrically. The gaseous ozone was contained in a tube 1 metre long closed by plates of quartz or rock salt. For small concentrations the absorption reached to about 316 $\mu\mu$ in the ultra-violet, but as the concentration increased, new bands appeared and extended into the region of longer wavelength. Liquid ozone did not show any absorption bands in the visible spectrum, but only a masking of the region of long wavelength to about 500 $\mu\mu$, and there were no bands in the ultra-violet, but the absorption extended into the visible spectrum as the concentration increased, but not so far as in the case of the gas. Some new bands were discovered in the red portion, which were only visible, however, when about three-quarters of the ozone had evaporated; they were also the first to disappear, and the pressure increased when this occurred. Determinations of the density (1.78, 1.75, and 1.83) and changes of pressure appeared to show the presence of a higher molecular modification of oxygen. E. W. W.

Spectroscopic Researches on Copper and Cobalt Solutions. B. E. MOORE (*Zeit. physikal. Chem.*, 1906, **55**, 641—682. Compare Donnan and Bassett, *Trans.*, 1902, **81**, 939; Hartley, *Trans.*, 1903, **83**, 401; Lewis, *Abstr.*, 1905, ii, 509; Jones and Bassett, *ibid.*, ii, 509).—The author has studied the absorptive power over a large part of the spectrum of dilute and concentrated solutions of copper chloride, sulphate, nitrate, and acetate, and cobalt chloride, sulphate, and nitrate. The manner also in which the absorption in these solutions is affected by adding acids and salts with a common ion has been investigated.

In confirmation of Ostwald's rule, very dilute salt solutions containing the same coloured ion yield the same absorption spectrum, independently of the nature of the negative ion in the salt. The repression of the dissociation produced by the addition of salts and acids with a common ion is accompanied by a distinct alteration in the absorption spectrum. The observations made by the author furnish no proof of the existence of hydrate molecules in solution, none at least for the existence of such hydrate molecules as are, in regard to absorption, quite distinct from the non-hydrated salt molecule; at the same time, physical aggregates of salt and water may exist in the solution. The existence of complex ions of copper and cobalt is rendered very probable (compare Donnan and Bassett, *loc. cit.*). A change of solvent causes displacement of the absorption bands for a given salt, and it is possible that some peculiarities in the absorption spectrum of concentrated acid solutions of cobalt chloride and sulphate, as compared with the spectra of pure aqueous solutions of these salts, may be due to the concentrated acid acting virtually as another solvent.

J. C. P.

Cathodic Phosphorescence of Europium diluted with Lime. Study of the Phosphorescent Ternary System: Lime—Gadolinia—Europia. GEORGES URBAIN (*Compt. rend.*, 1906, **142**, 1518—1520. Compare *Abstr.*, this vol., ii, 138).—The spectrum of the system lime—europia is described in detail. Europia—gadolinia mixtures when diluted with lime give the same bands. As the proportion of europia in the mixture is diminished, certain bands exhibit considerable alterations in relative intensity, and at very small concentrations new bands make their appearance.

Ternary mixtures of lime, gadolinia, and europia, in which the ratio of europia to gadolinia varied from 6 : 94 to 0·08 : 99·92, and the ratio of europia + gadolinia to lime from 1 : 99 to 5 : 95, were examined. The mixtures containing the smallest proportion of europia gave in all cases the spectrum of the binary system europia—gadolinia, whilst those containing the largest proportion of europia gave that of the system europia—lime provided the percentage of europia + gadolinia in the ternary mixture was less than four. When the proportion of europia + gadolinia was greater than 4 per cent., the spectra of both systems appeared. The observations indicate that the gadolinia or the lime may act as diluent of the europia, and that this is determined by the composition of the ternary mixture.

H. M. D.

The Theory of Fluorescence. GERTRUD WOKER (*J. Physical Chem.*, 1906, 10, 370—391).—Fluorescence is sometimes masked owing to the colour being similar to the colour of the substance, or more frequently when it is complementary. This may be seen by the extinction of the fluorescence of quinine sulphate by the addition of picric acid, and numerous other examples are given. It follows, therefore, that in general colour in compounds weakens or destroys fluorescence whether the colour is due to chromophores or impurities. A solvent can also have the same effect by displacing an absorption band towards the red end of the spectrum. Salt-forming groups also, and for the same reason, generally reduce fluorescence, a notable exception being the amino-group, which causes displacement towards the violet and generally increases fluorescence. The fluorescence of the xanthenes and flavones is considered, and a rule obtained, which appears to be general, that the fluorescence is most marked when a salt-forming group is in the furthest position from the chromophore. The fluorescence may lie too far out in the violet to be visible; in such a case, the causes which destroy a fluorescence visible previously may cause this to become visible, and it may therefore be developed by solution in a solvent of high dispersive power or by the addition of a chromophore. Another method for the development of fluorescence is the union of benzene radicles in definite ways, the most important being the union of phenyl groups in the ortho-position or in an analogous way.

L. M. J.

Dependence of the Action of Fluorescent Substances on their Concentration. A. JODBLAUER and HERMANN VON TAPPEINER (*Chem. Centr.*, 1906, i, 1792—1793; from *Arch. klin. Med.*, 86, 466—478).—The liberation of iodine from potassium iodide and the destruction of the active power of invertin by fluorescein increases to a maximum at 1:2000 mols. as the concentration of the fluorescein decreases and then begins to decrease slowly. Similar results are obtained for the Eder reaction (*Abstr.*, 1905, ii, 565). These facts do not agree with Straub's observations (*Abstr.*, 1904, i, 896), but resemble those found in the action of fluoresceins on dyes and leucobases of this series (Gros, *Abstr.*, 1901, ii, 433). The behaviour of methylene-blue is similar, the maximum being attained at a concentration of 1:2000 mols. The action of sodium dichloroanthracenedisulphonate and of æsculin increases slowly with the concentration and then more rapidly, so that the maximum effect corresponds with the maximum concentration. The difference between the photochemical behaviour of eosin and sodium dichloroanthracenedisulphonate depends, perhaps, on the fact that in the ionisation of eosin a structural change takes place in the molecule ("quinonisation"), and that only the ions are photochemically active, whilst the dissociated and undissociated portions of sodium dichloroanthracenedisulphonate have the same structure and are also probably equally active.

The therapeutic application of the above substances is also discussed in the original paper.

E. W. W.

Relation between the Photochemical Action of Substances of the Fluorescein Series and their Intensity of Fluorescence and Sensitiveness to Light. HERMANN VON TAPPEINER (*Chem. Centr.*, 1906, i, 1793—1794; from *Arch. klin. Med.*, 86, 478—486).—Experiments on the action of fluorescein and its halogen substitution derivatives on potassium iodide have shown that the quantity of iodine liberated in the presence of light is almost the same in all cases. The activity must be independent, therefore, of the sensitiveness to light of the fluorescein. These facts, taken in conjunction with the results of E. and H. W. Vogel's work, show that there is a considerable difference between the sensitising action of fluorescein on silver bromide gelatin plates and its action on potassium iodide in aqueous solutions. The photochemical action of fluorescent substances in aqueous solutions is not dependent on their decomposition by light. These phenomena are therefore to be regarded as catalytic actions and the fluorescent substances as light-catalysts.

In the case of invertin, however, the substitution derivatives of fluorescein have not the same effect. The action increases from fluorescein and tetrachlorofluorescein, which are completely inactive when the exposure to daylight is short, to tetrachlorotetraiodofluorescein, that is, in the order of decreasing fluorescence. The sensitising action increases irregularly as the brilliance of the fluorescence decreases.

The photochemical action of micro-organisms depends on the permeability of the membrane, and can only take place around the molecules which have passed through. A combination of the fluorescent substance with the enzyme is possibly necessary. E. W. W.

Chemical Action of Ultra-violet Light. W. H. ROSS (*J. Amer. Chem. Soc.*, 1906, 28, 786—793).—A study has been made of the rate of chemical action induced by ultra-violet rays emitted by an electric spark passing between aluminium terminals. The rate of decomposition of the iodides when aluminium terminals were used was found to be at least twice as great as that produced by the use of terminals of any of the other common metals. The effect of the ultra-violet light was determined by placing the solution in a small, shallow dish provided with a quartz cover. When the dish was placed beneath the spark, the amount of decomposition represented the total effect of the waves of light given out by the spark. By subtracting from this the amount of decomposition produced when a thick glass plate was interposed between the spark and the solution, the effect of the ultra-violet light alone, or that part of it capable of being absorbed by the glass, was determined. It was found that all the wave-lengths below $\lambda 3260$ were absorbed by the glass.

In the case of potassium iodide solution, it was found that the amount of iodine set free in a given time varied inversely as the square of the distance of the solution from the spark. In order to ascertain the influence of concentration, solutions were tested varying from $3N$ to $N/1000$, and it was found that the weaker the solution, the smaller was the amount of iodine liberated. On varying the time of

exposure, the amount of iodine set free was not at first exactly proportional to the time; this was doubtless due to the change in the colour of the solution, or its power of absorption, after a short exposure. When the glass plate was interposed, only a very small amount of iodine was liberated. The iodides of sodium, lithium, barium, calcium, and zinc gave the same results as potassium iodide at a temperature of about 18° . A variation of the temperature between 15° and 30° produced no appreciable change in the rate of decomposition.

Ferric salts are reduced by ultra-violet light, and the amount of the reduction is largely increased by the presence of sugar. The quantity of ferric salt reduced is approximately proportional to the time of exposure. A variation in the temperature of the solution has only a slight effect on the rate of reduction.

Solutions of chlorates and bromates are also reduced by ultra-violet light but, unlike the iodides or ferric salts, a variation in the strength of the solution from $N/2$ to $N/50$ does not appreciably affect the amount of the reduction. The chlorates undergo a greater reduction than the bromates and, in each case, the amount reduced varies directly with the time of exposure. The addition of sugar to the solutions causes an increased amount of reduction, and under these conditions the bromates are more largely reduced than the chlorates. E. G.

Kinetics of Photochemical Reactions. I. Reaction between Chlorine and Benzene in Light. EMANUEL GOLDBERG (*Chem. Centr.*, 1906, i, 1693; from *Zeit. wiss. Photograph. Photophysik. Photochem.*, 4, 61—95).—In experiments on the action of chlorine on benzene in light, the reacting substances contained in a closed vessel with parallel thin glass sides were stirred, and illuminated by an arc lamp or a Schott's uviol lamp. The velocity of chlorination of benzene is not a simple function of the concentration of the chlorine, but depends on the initial content of chlorine; when the latter is increased, the velocity becomes greater as the quantity of chlorine decreases. The increase of velocity cannot be due to rise of temperature caused by increased absorption of light, and the products of the reaction have no effect. As the reaction proceeds, the absorption spectrum does not show a change, which would indicate the formation of an intermediate compound.

It was found that the effects were caused by the presence of oxygen, which retards the chlorination of benzene in light. The solubility of oxygen in benzene at 25° is 0.185. Benzene, which does not contain oxygen, is rapidly chlorinated when exposed to the light of the uviol lamp. Oxygen appears to have the same effect in all cases of photochemical chlorination. The phenomena of photochemical induction and "deduction" are also due to the same cause. The marked effect of rise of temperature is due to the decrease of the solubility of oxygen in benzene, and in order, therefore, to prepare hexachlorobenzene the benzene should be boiled.

The chlorination of toluene, xylene, or acetic acid is also retarded by oxygen. E. W. W.

Reaction between Chromic Acid and Quinine in Light. EMANUEL GOLDBERG (*Chem. Centr.*, 1906, i, 1693—1694; from *Zeit. wiss. Photograph. Photophysik. Photochem.*, 4, 95—107. Compare preceding abstract).—Experiments on the action of chromic acid on quinine in light have been made by means of the apparatus described above.

The velocity of the reaction is proportional to the intensity of the light, and the results confirm Grotthus' law that only those rays are active which are absorbed. Beer-Lambert's simple absorption law also holds for the solution of chromic acid. The temperature-coefficient $K_T + 10/K_T$ is very small for photochemical reactions, the mean value for seven reactions being only 1.15. Ostwald's theory that photochemical reactions are analogous to "anactinic" reactions at very high temperatures appears therefore to hold. E. W. W.

Relation between Translation and Radiation Intensity of Positive Ions. JOHANNES STARK (*Chem. Centr.*, 1906, i, 1642; from *Physikal. Zeit.*, 7, 251—256).—The line spectrum of mercury vapour is caused by positive ions. The pressure of radiation brings about an equilibrium between the energy of radiation and the kinetic energy of the gas. The emission of light by the canal rays is due to their kinetic energy. The intensity of radiation in a state of equilibrium is proportional to the square of the velocity of translation. As the translation velocity of the positive hydrogen ions increases, the intensity of radiation of the shorter waves increases more rapidly than that of the longer. Positive ions are formed by the action of flame, impact of cathode rays, &c., and high velocity is imparted to them by rise of temperature, increase of current, or combustion. The line spectrum produced at a moderate temperature in the positive column or in the negative glow does not correspond with a state of equilibrium between emission and translation.

The spectrum of mercury is caused by uni-, bi-, and multi-valent ions. Lines formed by univalent ions (such as 2537) have at a comparatively small velocity (temperature of Bunsen flame) considerable intensity, whilst those due to bivalent ions appear at a high temperature. When the pressure of the mercury arc is raised, the intensity of the line 4078, produced by multivalent ions, increases more rapidly than that of the line 4047, emitted by bivalent ions. A greater energy of translation is required to produce a line spectrum in nitrogen than in hydrogen. E. W. W.

Spectrum of Helium from Radium Bromide. FRIEDRICH GIESEL (*Ber.*, 1906, 39, 2244. Compare Abstr., 1905, ii, 496).—Since the publication of the author's last paper on this subject, the amount of helium in the tubes examined has increased. Photographs are appended. A. McK.

Separation of Radium C from Radium B. F. VON LERCH (*Ann. Physik*, 1906, [iv], 20, 345—354. Compare Abstr., 1905, ii, 790).—Pieces of platinum foil with induced radioactivity are boiled with strong acid. It is then found that by immersing metals in the active

solutions so obtained, or by electrolysis of these solutions, radium *C* can be separated from radium *B* in the same way as thorium *B* has been separated from thorium *A* (see *loc. cit.*). Thus, radium *C* is precipitated on copper and nickel, and may also be precipitated at a bright platinum cathode by electrolysis with small current density.

If barium nitrate and then sulphuric acid are added to an active hydrochloric acid solution obtained as above, radium *B* is carried down with the barium, radium *C* is found in the filtrate. If copper is precipitated from a similarly active solution with potassium hydroxide, it carries down radium *C* and a part of radium *B*; the rest of the radium *B* is in the filtrate.

The activities of radium *B* and radium *C* decay to half their values in 26.7 and 19.5 minutes respectively (compare Bronson, *Abstr.*, 1905, ii, 567). J. C. P.

Action of Radium Rays on Mixtures of Hydrogen and Chlorine and of Hydrogen and Oxygen. WILLEM P. JORISSEN and WILHELM E. RINGER (*Ber.*, 1906, 39, 2093—2098. Compare *Abstr.*, 1905, ii, 219).—The previous experiments have been repeated with an improved form of apparatus and a larger quantity of radium bromide. The observed irregularities were due to varying temperatures in different parts of the apparatus.

With mixtures of hydrogen and oxygen, a reaction could not be observed seventy-one hours after the introduction of the radium bromide into the inner blackened tube. The disagreement between this result and those of Davis and Edwards (*Abstr.*, 1905, ii, 448) is due to the feeble penetrating power of the α -rays, which are those most effective in promoting ionisation. C. S.

Radioactivity of the Gases evolved from the Waters of Thermal Springs. PIERRE CURIE and A. LABORDE (*Compt. rend.*, 1906, 142, 1462—1465. Compare *Abstr.*, 1904, ii, 461).—The previous experiments have been extended to several new thermal springs. In consequence of an error in the calibration of the measuring apparatus, the numbers previously recorded for the quantity of emanation contained in the waters and in the gases evolved, require to be corrected. A table containing the corrected values and the new data is appended. H. M. D.

Radioactivity of Ashes and Lava from the Recent Eruption of Vesuvius. AUGUST BECKER (*Ann. Physik*, 1906, [iv], 20, 634—638).—The radioactivity of the products of the eruption appears to be less than that of most of the layers of the earth's crust. J. C. P.

Temperature Gradients of the Earth on the Hypothesis of Radioactive and Chemical Processes. JOHAN G. KOENIGSBERGER (*Chem. Centr.*, 1906, i, 1646; from *Physikal. Zeit.*, 7, 297—300).—The heat evolved by the disintegration of radium is sufficient to account for the temperature gradient. The disintegration of radium must

cease at higher temperatures; rise of temperature is conducive to the formation of radium β with absorption of heat.

Various theories of the heat of the earth are treated mathematically in the original paper. The variation of temperature with depth is not explained by Fourier's hypothesis. It is more probable that a portion of the heat is due to radioactive substances, and that the production of heat decreases rapidly with depth. The volcanic products are not more radioactive than sedimentary rocks formed at the surface.

E. W. W.

Spectrum of the Nitrogen Glow produced by the Rays of Radiotellurium. BERNHARD WALTER (*Ann. Physik*, 1906, [iv], 20, 327—332. Compare Sir William and Lady Huggins, *Abstr.*, 1904, ii, 4; Walter and Pohl, this vol., ii, 2).—Whilst the spectrum of the nitrogen glow caused by radium coincides with the spectrum of the negative glow in a Geissler tube containing rarified air, the spectrum of the nitrogen glow caused by polonium is more similar to the spectrum of the positive glow in such a tube.

J. C. P.

The most probable Value of the Ratio (ϵ/μ_0) of the Charge to the Mass of the Electron in Cathode Rays. CHARLES E. GUYE (*Arch. Sci. phys. Nat.*, 1906, [iv], 21, 461—468).—The determination of the ratio of the charge to the mass of the electron is obtained from the two equations, (1) $\frac{1}{2}\mu v^2 = U\epsilon$, and (2) $\rho = v\mu/H\epsilon$, where v is the velocity of the electron, U the potential of discharge, H the intensity of the magnetic field producing curvature of the rays of radius ρ . The results lead to the value 1.892×10^7 , which is not in accord with the value 1.858×10^7 obtained by Kaufmann. The values of μ in (1) and (2) are, however, only equal if the velocity is sufficiently small, and the author deduces a correction factor which reduces to $(1 - \beta^2/5)$, where β is the ratio of the velocity of the electron to that of light. The first value given above then reduces to 1.878×10^7 .

L. M. J.

Photoelectric Effect and Fall of Potential at an Alkali Electrode in Argon, Helium, and Hydrogen. H. DEMBER (*Ann. Physik*, 1906, [iv], 20, 379—397).—For the pressures commonly employed in measurements of potential fall, the photoelectric sensitiveness of the alloy containing potassium and sodium in atomic proportions is greater in helium than in hydrogen. This is true also when the ultra-violet rays are cut off. For higher potentials, the photoelectric sensitiveness of the potassium-sodium alloy is greater in argon than in helium. There is a general parallelism between the magnitude of the photoelectric effect and the fall of potential in the cases investigated.

J. C. P.

Change of Resistance of Palladium Wires caused by Occlusion of Hydrogen. FRITZ FISCHER (*Ann. Physik*, 1906, [iv], 20, 503—526. Compare Krakau, *Abstr.*, 1896, ii, 5; McElfresh, *Proc. Amer. Acad.*, 1904, 39, No. 14).—The resistance of a palladium wire increases immediately and rapidly with the first quantities of hydrogen

occluded. Onwards from the point at which the wire has absorbed thirty times its own volume of hydrogen, the increase is proportional to the quantity of occluded gas, as indicated by the formula $w/w_0 = a + bH$, where w_0 is the initial resistance of the palladium wire, w its resistance when it has absorbed H times its own volume of hydrogen, $a = 1.0292$, and $b = 0.000668$. The maximum value of the ratio w/w_0 which can be reached is 1.69.

The linear extension of a palladium wire due to the occlusion of hydrogen is up to the point of saturation proportional to the quantity of absorbed gas. When a charged palladium wire is freed from its occluded hydrogen, it is found to be shorter than it was originally in the uncharged condition, but its resistance is the same. J. C. P.

Free Energy of Some Halogen and Oxygen Compounds Computed from the Results of Potential Measurements. M. DE K. THOMPSON (*J. Amer. Chem. Soc.*, 1906, 28, 731—766).—If the saturated solution of a salt in contact with the solid salt is electrolysed at a constant temperature between electrodes consisting of the decomposition products, and if the process is reversible, the work done is that required to decompose the solid salt. Conversely, the energy obtainable from the combination when working reversibly as a voltaic cell is the free energy of formation of the solid compound from its constituents. Thus, the free energy change attending the formation of silver chloride could be determined either by measuring the decomposition potential between platinum electrodes of a saturated solution of the salt in water or by measuring the potential of the cell Ag/saturated solution of AgCl/Cl. The *E.M.F.* of such a cell is made up of the *E.M.F.*'s at the two electrodes. In many cases these separate values have been measured against a standard electrode and are recorded in the literature. Such data as are available have now been collected and united so as to obtain the *E.M.F.* of a cell composed of the elementary electrodes and a solution of the particular salt, and from the results thus obtained the free energy of the salt has been calculated.

The free energy has also been calculated from the electrolytic potentials of the elements of a compound and its solubility.

By these two different methods, the free energies of the chlorides, bromides, and iodides of silver, mercury, copper, thallium, and lead, of the oxides of silver and mercury, and also of water, ammonia, hydrogen chloride, and hydrogen bromide at about 18° have been computed, and the results are tabulated. The two series of values are in good agreement except in the case of silver and mercurous iodides. The disagreement in the latter cases is probably due to the existence of complex ions in the solutions of the iodides which affect the computation from their solubilities.

In the case of the solid halides, the chloride has a free energy which is 2.5—5.5*K* per equivalent greater than that of the corresponding bromide, and the bromide has a free energy 7—11*K* per equivalent greater than that of the corresponding iodide.

The corresponding mercurous, silver, and cuprous halides have free energies which differ from each other by less than 3.5*K* per equivalent,

but which increase slightly in every case in the order mercury, silver, copper.

The most important general conclusion drawn from the results is that the ratio of the free to the total energy of the solid salts, when these energies are referred to those of the elements in the solid state as zero, does not differ from unity by more than 7 per cent. except in the case of silver iodide. For gaseous water and hydrogen chloride produced from the gaseous elements, the ratio of free to total energy is not far from unity, but has widely divergent values in the case of hydrogen bromide and ammonia, indicating the absence of any simple relations.

E. G.

Spontaneous Ionisation of Air and Other Gases. HANS GEITEL (*Chem. Centr.*, 1906, i, 1772; from *Naturw. Rundsch.*, 21, 221—225. Compare this vol., ii, 329).—Pure dry air has the greatest dispersive power. Whilst the dispersion is the same for both kinds of electricity in flat regions, in mountainous districts the dispersion of negative electricity is far greater than that of positive. The concentration of positive ions is especially great at the summits of mountains. These considerations in conjunction with the phenomena of saturation currents and the loss of conductivity caused by a weak electric field appear to indicate that ordinary or normal air is ionised to a certain extent.

E. W. W.

Conductivity of Air in Contact with Autoxidising Substances. WILLEM P. JORISSEN and WILHELM E. RINGER (*Ber.*, 1906, 39, 2090—2093. Compare Abstr., 1905, i, 354; Schenck, Mihr, and Banthien, this vol., ii, 326).—The ionising effect of triethylphosphine, benzaldehyde, turpentine, and phosphorus on air was determined by noting the time required for a charged rod, connected with an electrometer and dipping into an enclosed volume of air, to alter its potential by a definite amount. In the presence of each of the first three substances, the conductivity of the air is diminished, but in the presence of phosphorus it increases to four times the normal value.

C. S.

Introduction of the Conception of the Solubility of Metal Ions with Electromotive Equilibrium. ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 2—9).—A bar of metal, for instance, zinc, in a solution of a salt of the metal sends into the solution exclusively ions with a positive charge, causing the surrounding solution to become electro-positive and the zinc itself electro-negative, and forming the so-called electric double layer. It is possible theoretically to give such a concentration to the metal ions in a solution that on immersing the corresponding metal in it, neither the metal nor the solution becomes electrically charged. To calculate the solubility of the ions = K , the expression

$$\Delta_0 = 0.0578/v \cdot \log K (55.5v + 1)$$

is used, Δ_0 denoting the electrode potential and v the valency of the metal.

The values of K are given for a number of metals, with potassium,

sodium, barium, calcium, magnesium, aluminium, zinc, iron, &c. K is greater than 1, indicating that even in the most concentrated solutions of the corresponding salts the metal ions will not have reached their concentration of saturation. In the case of copper, where K has the value 10^{-23} , the concentration of the copper ions is greater than that of saturation, and copper ions will be deposited on a copper bar when it is immersed, in consequence of which the bar becomes charged with positive and the solution with negative electricity.

E. F. A.

Hydration of the Ions. I. GUSTAV BUCHBÖCK (*Zeit. physikal. Chem.*, 1906, **55**, 563—588).—An attempt to determine the extent to which the ions of electrolytes are hydrated is made on the lines adopted by Nernst and his pupils (Abstr., 1901, ii, 12, 13). A solution of hydrochloric acid containing a non-electrolyte (mannitol or resorcinol) is electrolysed, and investigation shows whether during electrolysis a displacement of the water relatively to the non-electrolyte takes place. For this purpose, the author has determined the transport numbers of the hydrogen and chlorine ions in a specially devised apparatus with a platinum cathode and a silver anode. In this arrangement, the processes going on at the electrodes result in a dilution of the solution, and the electrodes are, therefore, placed at the top of each limb of the U-shaped apparatus. Into the upper part of each limb there is ground a short piece of glass tube, whilst the limb itself is widened out at the top. Into the annular cup space so formed the electrodes are placed. The anode and cathode compartments can be shut off by taps, and the U-tube itself consists of two halves united by a ground joint.

The mannitol in the solutions was accurately estimated by precipitating the hydrochloric acid with silver carbonate, removing any dissolved silver with hydrogen sulphide, and then evaporating to dryness. To estimate the resorcinol in the hydrochloric acid solutions, salt was added and repeated extractions with ether were made. From the ethereal solution, the resorcinol was obtained by passing a current of air through the gently warmed solution, and finally a current of dry hydrogen at 139° .

The experiments show that water does indeed move with the ions, and it was found that the relative hydration of the two ions varies with the concentration of the added non-electrolyte and with the concentration of the hydrochloric acid. It is curious that the ratio x/y (where x and y are the numbers of water molecules associated with H^+ and Cl^- respectively) is diminished by mannitol and increased by resorcinol, but extrapolation leads in both cases to the same value of the ratio for a solution which is infinitely dilute with respect to the non-electrolyte. Probably the molecules of mannitol and resorcinol are capable, like the water molecules, only to a very much smaller extent, of associating themselves with the moving ions. The value of the ratio x/y diminishes with falling concentration of the hydrochloric acid, and it is probable that for an infinitely dilute solution $y = 4$, if it is assumed that $x = 1$.

J. C. P.

Electrochemical Equivalent of Silver. K. E. GUTHE (*Ann. Physik*, 1906, [iv], 20, 429—432).—From the author's latest work it follows that the electrochemical equivalent of silver is 1.11773 mg. per coulomb for the porous cell coulometer and 1.11815 mg. per coulomb for the filter paper coulometer.
J. C. P.

Magnetic Properties of Compounds of Boron and Manganese. ARMAND BINET DU JASSONEIX (*Compt. rend.*, 1906, 142, 1336—1338).—The author has examined the magnetic properties of the compounds of boron and manganese obtained by reducing the oxides of manganese by means of boron in an electric furnace (Abstr., 1905, ii, 90). Owing to the difficulty of fusing the compounds without oxidation, they were finely powdered and sifted, and the effects of introducing a tube containing equal weights of the powder into a magnetic coil were measured; the results show that of the two compounds, MnB and MnB_2 , the first only has magnetic properties, and the magnetic properties of other mixtures of boron and manganese are due to the presence of this compound.
M. A. W.

Condition of Benzene Derivatives as Deduced from the Magnetic Rotation. HUGO KAUFFMANN (*Zeit. physikal. Chem.*, 1906, 55, 547—562. Compare Abstr., 1901, i, 318).—The author's earlier work has led him to the view that the condition of a benzene derivative may vary. Among the various conditions possible is one which the author calls the *D* condition, because it is best interpreted by Dewar's benzene formula. In this condition a benzene derivative exhibits the following characteristics: (1) maximum reactivity, (2) maximum tendency to pass by oxidation into substances of a quinone-like nature, (3) maximum power to show violet luminescence, rendered evident by Tesla rays in the case of the vapour, (4) maximum abnormality in the magnetic rotation. By way of further characterising this *D* condition, it is shown in the present paper that certain compounds exhibiting violet fluorescence give abnormally high values of the magnetic molecular rotation. Introduction of the carbethoxy- or methoxy-group into the nucleus of a substance which is in the *D* condition renders that condition still more marked. The presence of an ethylene linking has the same effect in the case of styrene derivatives, but the opposite effect in the case of stilbene derivatives. In accordance with previous observations, colour and the *D* condition are opposed to each other; the abnormality in the magnetic molecular rotation is much smaller for coloured compounds. The further the nucleus of a benzene derivative is removed from the *D* condition, the more likely is it that the introduction of auxochromes will affect it in the direction of the *D* condition; if, on the other hand, the benzene derivative is already markedly in the *D* condition, as in the case of stilbene, the introduction of auxochromes may have the contrary effect.

Abnormality in magnetic rotation is considered to be of as great importance in the characterisation of benzene derivatives as conductivity is in the case of electrolytes.
J. C. P.

Simple Sensitive Thermometer for Low Temperatures. ALFRED STOCK and CARL NIELSEN (*Ber.*, 1906, 39, 2066—2069).—Temperatures between -183° and -200° can be easily and rapidly determined to within 0.01° by means of the apparatus described and sketched in the paper. The principle of the method is the measurement of the vapour pressure of liquid oxygen; the relation between the vapour pressure of liquid oxygen and the temperature is ascertained from a curve drawn from the mean of the results of various workers.
C. S.

Regulator for Alternate Heating and Cooling. ANTOINE VILLIERS (*Ann. Chim. anal.*, 1906, 11, 177—180).—This is a variety of thermostat regulator in which the gas supply is delivered at the bottom of a glass tube, *A*, from which it reaches the burner by two passages, (1) through a hole higher up the side of the tube *A*, (2) through a siphon tube *B*, starting from near the bottom of *A*. As the liquid in the reservoir of the regulator expands, the mercury is pushed before it and first closes the end of *B*, then gradually rises in *B*, ultimately overflowing into *A* and closing the end of the gas delivery tube. The bath now commences to cool, the mercury falls, and presently the siphon tube empties itself, so that the gas again reaches the burner by both passages. The net result is that the temperature of the bath rises and falls alternately between two limits.
J. C. P.

Periodic Interrupter. ANTOINE VILLIERS (*Ann. Chim. anal.*, 1906, 11, 181).—When it is desired to heat a liquid at intervals, it may be put in the reservoir of the regulator described in the previous abstract. The reservoir may be made of glass and heated in a bath, or of copper and heated directly.
J. C. P.

Specific Heat of Chromium, Sulphur, Silicon, and some Salts between -188° and the Ordinary Temperature. CARL FORCH and PAUL NORDMEYER (*Ann. Physik*, 1906, [iv], 20, 423—428).—The method used in determining the specific heat was similar to that employed recently by Dewar, and consisted in introducing the substance into a weighed quantity of liquid air and finding the consequent loss of weight. The salts taken were the sulphates of copper, iron, potassium, and ammonium, the nitrates of sodium and ammonium, mercurous and mercuric chlorides, potassium oxalate, and *d*-tartaric acid. In these cases it was found that the greater the specific heat, the more marked was its decrease with falling temperature. The elements named in the title also exhibit a decrease in their specific heat as the temperature falls. The behaviour of silicon at low and medium temperatures as regards variation of specific heat is somewhat similar to that of carbon and boron at high temperatures.
J. C. P.

Solidification of Inorganic Salts and Salt Mixtures. I. Solidification of Pure Salts and the Accompanying Thermal Effects. WILHELM PLATO (*Zeit. physikal. Chem.*, 1906, 55, 721—737. Compare Ruff and Plato, *Abstr.*, 1903, ii, 588).—A crucible containing

a pure fused salt is placed in an electric oven, which is allowed to cool regularly by altering gradually and regularly the current which heats the oven. From the cooling curve observed for the salt under these conditions, it is possible to deduce the latent heat of fusion and the specific heat of the salt, provided these constants may be assumed as known for another salt, the cooling curve for which must be determined under the same conditions. The values thus obtained for the latent heat of fusion and the specific heat agree well with those determined directly.

J. C. P.

Determination of High Temperatures by means of Chemical Equilibrium and the Laws of Thermodynamics. H. VON WARTENBERG (*Chem. Centr.*, 1906, i, 1727; from *Ber. Deut. phys. Ges.*, 4, 97—103).—If the conditions of a chemical equilibrium are known exactly for a certain temperature, the heat of reaction q and its temperature-coefficients, then the formula $d/d\log.kT=q/RT^2$ may be applied to the estimation of temperatures. The dissociation of water has been investigated between 1400° and 2300° . The lower temperatures were determined by thermoelectric methods; at higher temperatures, a Wanner pyrometer was used. The dissociation was determined by Löwenstein's method by means of iridium; 1.18 and 1.77 per cent. were dissociated at 2155° and 2257° , absolute temperatures respectively. Holborn's determinations of specific heat were used. The calculated and observed temperatures showed a maximum difference of 1.5 per cent. at 1400° absolute. At 2000° , a rise of temperature of 1° affected the dissociation by 0.5 per cent., whilst the air thermometer showed a difference of only 0.05 per cent. The differences between the calculated and observed values are mostly in one direction, probably because Holborn's determinations of the specific heats were too low; Langen found much higher values, and by assuming intermediate values a much closer agreement may be obtained.

E. W. W.

Relation of Heat of Vaporisation to Boiling Point. EUGENE C. BINGHAM (*J. Amer. Chem. Soc.*, 1906, 28, 723—731).—The heats of vaporisation of a large number of substances have been calculated by means of Nernst's formula, $\lambda/(1-p/\pi)=R(T_1T_2/T_1-T_2)\log.(p_1/p_2)$, where R is the gas constant, π the critical pressure, and p, p_1, p_2 are the vapour pressures at the temperatures T, T_1, T_2 respectively, and where T_1 and T_2 are taken so near together that the arithmetical and geometrical means are practically identical. The results thus obtained agree well with the observed values.

It is shown that the values of Trouton's constant increase regularly and in accordance with the equation $\lambda'/T_0=17+0.011T$. For associated compounds, the values of λ'/T_0 are considerably larger than the normal value $17+0.011T$, and the difference between these two quantities is considered to be a measure of the association.

E. G.

Researches on Vapour Pressure. HANNS VON JÜPTNER (*Zeit. physikal. Chem.*, 1906, 55, 738—752. Compare Guye and Mallet, *Abstr.*, 1902, ii, 243).—Van t Hoff's empirical formula $\log.\pi=f(1-1/\theta)$, in which π and θ are corresponding pressure and temperature, and f is

a constant, is shown to be closely connected with the Clapeyron-Clausius equation and with Trouton's formula.

The value of f , as a matter of fact, varies with the substance investigated and with the temperature. With rising temperature, the value of f for a particular substance first falls, then reaches a minimum, and subsequently rises again. This minimum value of f , and the temperature θ for which it is observed, vary from substance to substance. In the first period, the falling off of f with the temperature may be represented by a straight line; in the second period, the increase of f with temperature may be represented by the arc of a circle. The f -curves for the monatomic elements mercury, argon, and xenon are almost coincident.

J. C. P.

The van't Hoff-Raoult Formula. WILDER D. BANCROFT (*J. Physical Chem.*, 1906, 10, 319—329).—It was explicitly pointed out by van't Hoff that the relation $PV=RT$ can only hold in a solution if the heat of dilution is zero; this, however, is seldom the case. Trevor has deduced for any fixed concentration the expression $PV=Q+Td(PV)/dT$, where Q is the heat of dilution—positive if heat is developed on dilution and given by the expression $C.dQ/dC$, where C is the number of molecules of solvent per molecule of solute. If Q is constant, then $PV=RT+A$; if $Q=A-BT$, then $PV=RT+A+BT\log T$, and other expressions could be deduced on the assumption that Q stands for other functions of the temperature. It is clear, however, that where Q is great the osmotic pressure will be high and apparent molecular weight will be low. This is seen to be the case for solutions of sodium in mercury, sulphuric acid in water, and other cases, whilst further for the two named the corrected values approximate to the normal. It is shown, however, that the abnormal results found for sodium chloride cannot be due to the heat of dilution. Whilst the effect of the heat of dilution does not affect solutions at infinite dilution, yet all determinations in finite solution must be in error to an extent varying from a fraction of a per cent. to several hundred per cent.

L. M. J.

Vapour Pressure and Chemical Composition. EUGENE C. BINGHAM (*J. Amer. Chem. Soc.*, 1906, 28, 717—723).—The vapour pressure curve can be calculated by means of an equation of the form $p/\pi = \int (T/\tau)$, where π and τ represent the critical pressure and critical temperature respectively. For the function $\int (T/\tau)$ Nernst has given the following expression:

$$\log \pi/p = 1.75 \log \tau/T + a' [\{(\tau/T) - 1\} - 1/2.36 \{1 - (T/\tau)\}],$$

where a' is a constant varying with the nature of the substance. A table is given of the values of a' and Ma' (where M is the molecular weight) for a large number of substances as calculated from their boiling points under atmospheric pressure and their critical data. It is found that the value of a' increases regularly in proportion to the complexity of the molecule, being smallest for hydrogen and greatest

for the associated alcohols of high molecular weight. It is shown that these values may be represented by an equation

$$M_a' = 42l + 1.9m + 41n + \dots$$

where l , m , and $n \dots$ are the number of atoms of the elements carbon, hydrogen, oxygen... respectively in the molecule. E. G.

Applicability of Raoult's Laws to Molecular Weight Determinations in Mixed Solvents and in Simple Solvents the Vapours of which Dissociates. GILBERT N. LEWIS (*J. Amer. Chem. Soc.*, 1906, 28, 766—770).—It is shown from theoretical considerations that Raoult's law for the lowering of the vapour pressure is applicable to an ideal dilute solution in any constant boiling mixture the vapour of which obeys the gas laws, and that the law for the elevation of the boiling point is applicable to an ideal solution in any constant boiling mixture whatever. E. G.

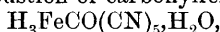
Molecular Aggregation of Liquefied Gases. MATTHEW A. HUNTER (*J. Physical Chem.*, 1906, 10, 330—360).—The lowering of the vapour pressure of a solvent is given by the expression $(p - p_1)/p_1 = n/N$, where p , p_1 are vapour pressures of solvent and solution, and n , N the number of molecules of solute and solvent. The author has conducted experiments on this subject with liquefied gases at low temperatures obtained by the use of liquid air. Diagrams and full description of apparatus are given. The only compounds which were found to dissolve readily and form homogeneous mixtures with liquid oxygen were ethane and ethylene. The former gave values for the lowering of the vapour pressure which were in accord with the calculated values, but with ethylene the experimental values were about three times too great, indicating therefore dissociation of the ethylene or association of the oxygen. In solutions in methane, ethylene gave normal results, but ethane gave values indicating dissociation or association of solvent. The gases carbon dioxide, hydrogen sulphide, acetylene, nitrous oxide, nitric oxide, hydrogen phosphide, and sulphur dioxide were found not to be soluble in either solvent to the extent of 1 per cent. In the course of the experiments, the vapour pressures at low temperatures were obtained for methane, ethylene, nitrous oxide, and acetylene, and the results are given. Experiments on solutions of ozone in oxygen were also undertaken, but it was found that the solutions give a constant boiling mixture of minimum boiling point at between 4 and 5 per cent. of ozone, and the molecular complexity of ozone could therefore not be found. An attempt to dissolve ozone in liquid nitrogen was also made, but when the last traces of oxygen were removed the ozone exploded with such violence that, as the author states, "no trace indeed of the platinum thermometer was to be found." L. M. J.

Formation of Endothermic Compounds at High Temperatures. MARCELLIN BERTHELOT (*Compt. rend.*, 1906, 142, 1451—1458).—The thermodynamic deduction that endothermic compounds should be formed at high temperatures is discussed. The author considers that the facts which are usually cited in support of this deduction are

not inconsistent with the general thermochemical rule which is in agreement with the great majority of chemical changes taking place at the ordinary temperature. A distinction should be drawn between truly endothermic compounds which are decomposed into their component elements in their usual physical state of aggregation with development of heat and those which are formed at high temperatures from their elements with development of heat. The variation of the sign of the heat change with the temperature is frequently determined by purely physical changes or polymerisation phenomena. The formation of ozone, nitrous oxide, nitric oxide, and of hydrogen peroxide from water and oxygen are changes which are only apparently endothermic. In the author's opinion there is no known example of the formation of an endothermic compound as the result of a rise of temperature pure and simple; other energy changes of chemical and electrical nature are always involved.

H. M. D.

Heat of Formation of Carbonylferrocyanic Acid. JOSEPH A. MULLER (*Compt. rend.*, 1906, 142, 1516—1517).—The measurement of the heat of combustion of carbonylferrocyanic acid,



in the calorimetric bomb gave as mean of seven determinations 809,800 cal. at constant volume. The products formed are nitrogen, carbon dioxide, water, and ferric oxide. The calculated heat of formation of the acid, $\text{H}_3\text{FeCO}(\text{CN})_5$, leaving out of account the heat of hydration, is -48,600 cal. The acid is therefore much less endothermic than ferrocyanic acid (heat of formation = -122,000 cal.), and this is attributed to the substitution of the exothermic group CO for the endothermic group HCN.

H. M. D.

Relation of Absorption to Surface Tension. A. CHRISTOFF (*Zeit. physikal. Chem.*, 1906, 55, 622—634. Compare Abstr., 1905, ii, 806).—The author has determined the absorption coefficient for hydrogen, nitrogen, oxygen, methane, and carbon monoxide in 95.6 per cent. sulphuric acid, and finds the values 0.0102, 0.01555, 0.02945, 0.03072, and 0.02164 respectively. These values are not very different from those obtained when water is taken as solvent, except in the case of hydrogen (absorption coefficient in water = 0.0193).

The solubilities of hydrogen, nitrogen, oxygen, methane, carbon monoxide, and carbon dioxide in 61.62 per cent. and in 35.82 per cent. sulphuric acid have also been determined, and the curves in which solubility is plotted against percentage of sulphuric acid all exhibit distinct minima, whilst the curve in which surface tension is plotted against percentage of sulphuric acid exhibits a distinct maximum (compare Whatmough, Abstr., 1902, ii, 127; Skirrow, *ibid.*, ii, 600). The lowering of solubility in the H_2O — H_2SO_4 mixtures is less marked for carbon dioxide than for the other gases, the solubilities of which are affected to about the same extent.

If the following liquids, water, aniline, nitrobenzene, benzene, toluene, acetic acid, chloroform, alcohol, and acetone, are arranged in the descending order of magnitude of their surface tension, they are in the ascending order of magnitude of their power to absorb carbon monoxide.

The product of surface tension and absorption coefficient is of the same order of magnitude for liquids of the most different character.

J. C. P.

Osmotic Pressure of Solutions of Non-electrolytes in connection with the Deviations from the Laws of Ideal Gases. JOHANNES J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 53—63. Compare Morse and Frazer, *Abstr.*, 1905, ii, 575).—In considering osmotic pressure results, the molecular volume of the solvent in the solution and not that of the whole solution must be taken into account. The author demonstrates that it is no longer possible to uphold the conception of osmotic pressure as due to the pressure of the molecules of the dissolved substance acting as a gas pressure.

The molecules of dissolved substance reduce the water to another state of concentration (less concentrated, owing to the breaking down of associated molecules), with the result that pure (partly associated) water of concentration 1 will move towards the water in the solution of concentration $1 - x$ in consequence of the impulse of diffusion.

A current of which the equivalent of pressure $= RT/V [-\log(1 - x)]$, where V is the molecular volume of the solvent, arises therefore in the neighbourhood of the semi-permeable membrane, and this current can only be checked by a counterpressure on the solution of equal value: this is the so-called osmotic pressure.

The impulse of diffusion might equally well be checked by cooling the solution, when the term "osmotic temperature" might be employed.

E. F. A.

Osmotic Pressure of Colloidal Ferric Hydroxychloride. G. MALFITANO (*Compt. rend.*, 1906, 142, 1418—1421. Compare *Abstr.*, 1905, ii, 459; 1906, ii, 33, 450; Duclaux, *Abstr.*, 1905, ii, 511).—When a colloidal solution of ferric hydroxychloride, obtained by heating at 115—120° a 0.5 per cent. solution of ferric chloride for fifteen minutes, is filtered through a collodion membrane under a pressure of 1.5 m. of water, the filtrate consists of a 1/1000*N* solution of hydrogen chloride and the residue contains 18 and 1.7 per cent. of iron and hydrogen chloride respectively; if 10 c.c. of this concentrated colloid is placed in a collodion sac and immersed in the filtrate, it absorbs the liquid until its volume is increased to 49 c.c., but no change in volume occurs if the colloid is previously diluted with the filtrate to the same extent. The pressure or the force of expansion of concentrated colloidal solutions separated by a semi-permeable membrane from the filtrate is not a function of the mobility of the granules, but is limited, and seems to depend on the quantities of the electrolyte retained by the granules and free in the filtrate.

M. A. W.

General Equations of the Theory of Solutions. JOSEPH E. TREVOR (*J. Physical Chem.*, 1906, 10, 392—412).—A mathematical paper, in which are deduced on the basis of thermodynamics the general equations of solutions, especially the case in which one component is not volatile. The treatment is clear and comparatively simple.

L. M. J.

Influence of One Substance on the Solubility of Another. MAX LEVIN (*Zeit. physikal. Chem.*, 1906, 55, 513—536).—The paper begins with a critical review of work already done on this subject, and this review shows that in general non-electrolytes have no appreciable influence on the solubility of other substances.

The author has himself studied the effect of sodium chloride, nitrate, and sulphate, lithium chloride and sulphate, ammonium chloride, sucrose, and dextrose on the solubility of picric acid. All the salts mentioned increase the solubility of picric acid, and the extent of the increase may be approximately calculated by Noyes' method (*Abstr.*, 1899, ii, 9). The relative magnitude of the influence of sulphate, chloride, and nitrate on the solubility of picric acid is pretty much the same as that of their influence on the solubility of non-electrolytes. The order of the different cations, however, arranged according to the magnitude of their influence on the solubility of picric acid, is somewhat different from what has usually been found, for the lithium salts have the greatest effect, and the difference between the sodium and ammonium salts is not great. The effect due to these salts is greater than that observed when an electrolyte and a non-electrolyte are concerned, so that a special influence must be attributed to the ions. The effect of sucrose and dextrose on the solubility of picric acid is not appreciable.

The author argues that the phenomena in question cannot be interpreted by reference to the theory of internal pressure, or to hydration in solution, or to the formation of complexes. The cause must be some interaction of the dissolved substances, and as non-electrolytes have practically no influence on the solubility of other non-electrolytes the interaction must be one in which the ions are concerned primarily. Further discussion leads to the conclusion that electrolytes cannot follow the mass action law at concentrations at which they have an influence on the solubility of other substances. The limiting concentration above which strong electrolytes affect the solubility of other substances and below which they may be expected to follow the mass action law is probably about $0.05N$.
J. C. P.

Organic Solvent and Ionising Media. V. Solvent Power. PAUL WALDEN (*Zeit. physikal. Chem.*, 1906, 55, 683—720. Compare *Abstr.*, 1904, ii, 227; this vol., ii, 149, 335, 336).—The question why a substance should be soluble in one liquid and not in another has received different answers; the author gives a *résumé* of these and discusses the various factors which bear on the relation of solvent and solute, such as polymerisation of the solvent molecules, dissociative power, and association of solvent and solute molecules. It is to be expected that for a given electrolyte as solute in different organic solvents the solubility will increase as the dissociative power of the solvent and the tendency to association increase.

To throw light on these relationships, the author has determined the solubility of tetraethylammonium chloride, bromide and iodide, tetramethylammonium chloride, bromide and iodide, tetrapropylammonium iodide, and several halides of the alkali metals in a large number of organic solvents at 0° and 25° . As regards the solubility of tetra-

ethylammonium iodide in twenty-three solvents, it appears that the temperature-coefficient is positive in all cases, and is greatest for the solvents containing the $-OH$ group. The greater the tendency to association on the part of the solvent, the greater is its solvent power. It appears also that a liquid with high dielectric constant has a greater solvent power than a liquid with low dielectric constant. Another interesting result obtained with tetraethylammonium iodide is that at 25° its solubility in a number of ionising solvents is such that the degree of dissociation in the saturated solutions has in each case about the same value, 0.48.

A comparison of the solubilities of tetramethylammonium iodide and tetrapropylammonium iodide with that of tetraethylammonium iodide in a number of solvents shows that the more complex the alkyl group in the cation the greater is the solubility in the various solvents. Further, for solvents belonging to the same homologous series, the solvent power diminishes as the series is ascended.

The solubilities of lithium, sodium, potassium, and rubidium iodides in furfuraldehyde have been determined, and are found to diminish from lithium iodide to rubidium iodide in the order given. On the other hand, when potassium chloride, bromide, and iodide are taken with the same solvent, the solubility increases with the molecular weight of the salt. The solubility of potassium iodide in numerous solvents has been determined, and it is found that the temperature-coefficient of solubility is negative except with the solvents water, ethylene glycol, methyl and ethyl alcohols. Investigation shows that some of the other alkali iodides have a negative temperature-coefficient of solubility in some solvents.

J. C. P.

Hydrolysis of Dichromates and Polymolybdates. JULIUS SAND (*Ber.*, 1906, 39, 2038—2041).—The value of $K = (H')^2(CrO_4'')^2/(Cr_2O_7'')$, the equilibrium constant for a solution of pure potassium dichromate in water, has been determined by mixing with potassium iodide and iodate and determining the velocity of iodine formation, which depends on the ionic concentrations of H' , I' , and IO_3' (compare Dushman, *Abstr.*, 1904, ii, 718).

If, when $t = 0$, $Cr_2O_7'' = A$, $IO_3' = B$, and $I' = C$, then $(Cr_2O_7'')_t = A - x$, $(IO_3')_t = B - x/3$, and $(CrO_4'')_t = 2x$, since $3Cr_2O_7'' + IO_3' + 5I' = 6CrO_4'' + 3I_2$.

If $C = 8A/3$ and $B = A/3$, then $K' = 1/t, 1/3A, x^3/(A - x)^3$.

At 25° and for $A = 0.07283$, constant values of $K' = 0.00627$ have been obtained.

J. J. S.

Colloids. ALFRED LOTTERMOSER (*Chem. Zeit.*, 1906, 30, 664—665).—A brief account of some of the more important characteristics of colloidal solutions.

P. H.

Supposed Alteration in the Total Weight of Substances taking part in a Chemical Reaction. HANS LANDOLT (*Zeit. physikal. Chem.*, 1906, 55, 589—621. Compare *Abstr.*, 1893, ii, 452; Heydweiller, *Ann. Physik*, 1901, 5, 394; Rayleigh, *Nature*, 1901, 64, 181; Joly, *Trans. Roy. Dublin Soc.*, 1903, 8, 23; Lo Surdo, *Abstr.*,

1904, ii, 720).—The author has resumed his earlier experiments (*loc. cit.*) with the aid of a new and very accurate balance. The maximum error of one operation is set down as 0.03 mg.; so that if an alteration of weight greater than this amount occurs in any of the reactions investigated, it cannot be attributed to experimental error. Of the various chemical reactions and processes of solution investigated, two are accompanied by a loss of weight well beyond the experimental error. These reactions are: (1) $\text{Ag}_2\text{SO}_4 + 2\text{FeSO}_4 = 2\text{Ag} + \text{Fe}_2(\text{SO}_4)_3$ or $3\text{AgNO}_3 + 3\text{FeSO}_4 = 3\text{Ag} + \text{Fe}_2(\text{SO}_4)_3 + \text{Fe}(\text{NO}_3)_3$, the loss here varying from 0.068 mg. to 0.199 mg. in nine experiments; (2) $\text{HIO}_3 + 5\text{HI} = 3\text{I}_2 + 3\text{H}_2\text{O}$, the loss varying from 0.047 mg. to 0.177 mg. in nine experiments. Taking into account also the other reactions in which a change of weight under or only slightly exceeding the maximum experimental error was observed, it is noteworthy that in only twelve out of fifty-four has an increase of weight been observed, and that increase is invariably slight (0.002–0.019 mg.). From an experiment in which an aqueous solution of cadmium iodide was electrolysed with alternating current, it appears that there is no connection between the loss of weight and the appearance or disappearance of electrons. In reference to the two cases in which a definite loss of weight was observed, it is suggested that the atoms (like those of radioactive elements) lose a small part of their mass in the reaction, and that those detached portions may escape through the walls of the containing vessel.

J. C. P.

Variations in the Affinity Value of Single Bonds. BERNHARD FLÜRSCHHEIM (*Ber.*, 1906, 39, 2015–2017. Compare *Abstr.*, 1903, i, 79; 1905, i, 614).—A reply to Werner (this vol., i, 436), and a claim for priority for Claus (*Abstr.*, 1881, 679).

G. Y.

Relative Strengths of Acids. PHILIP BLACKMAN (*Chem. News*, 1906, 93, 284).—The author advances a mathematical proof of the connection which exists between the relative strengths of acids and their molecular conductivities.

P. H.

Heterogeneous Equilibria: Formation of Phosphonium Chloride, Ammonium Carbamate, and Ammonium Hydrogen Sulphide. E. BRINER (*Compt. rend.*, 1906, 142, 1416–1418).—By means of the apparatus already described (this vol., ii, 424) the author has determined the equilibrium constant K and the dissociation pressure π for three heterogeneous systems each consisting of one solid and two gaseous phases.

For the system ($\text{HCl} + \text{PH}_3$), $\pi = 5.4$ and $K = 7.4$ at 0° , and the heat of formation q is 16 cal. In the system ($\text{CO}_2 + 2\text{NH}_3$) (compare Horstmann, *Abstr.*, 1876, ii, 269; 1877, i, 433; Isambert, *Abstr.*, 1882, 269), the melting point of ammonium carbamate, 152° , is a triple point, and $\pi = 2.2$ and $K = 1.5$ at 77.2° , the corresponding values at 98.5° being 6.4 and 39.05 respectively, whilst at 152° $\pi = 63.3$. In the system ($\text{NH}_3 + \text{H}_2\text{S}$) (compare Troost, *Abstr.*, 1879, 880; Isambert *Abstr.*, 1879, 880; 1883, 548), in the presence of excess of hydrogen sulphide, the melting point, 120° , of ammonium hydrogen sulphide is a

triple point, and $\pi = 0.09$ at 0° , and at 22° $\pi = 0.41$ and $K = 0.04$. In the presence of excess of ammonia the liquid compounds $(\text{NH}_4\text{HS} + n\text{NH}_3)$ are formed. M. A. W.

Examples of the Law of Partition. WALTER HERZ and MARTIN LEWY (*Chem. Centr.*, 1906, i, 1728; from *Jahr.-Ber. Schles. Ges. vaterländ. Kultur*, 1906, 1—9. Compare this vol., ii, 76).—The distribution of ammonia between water and chloroform or bromoform shows that ammonia forms a double molecule in these solvents. This is also the case with phenol in chloroform or bromoform, but in carbon tetrachloride or carbon disulphide triple or still more complicated molecules are formed. Acetone is bimolecular in carbon tetrachloride. The partition of acetone between water and chloroform does not give constant results, probably owing to the formation of a compound of acetone and chloroform which is decomposed by water. Formaldehyde is polymerised in aqueous solutions (Abstr., 1905, i, 589) and apparently to a greater extent in chloroform, but less so in amyl alcohol. The tendency of chloroform to induce polymerisation is in all cases much greater than that of amyl alcohol. Dimethylamine hydrochloride appears to form quadruple molecules in chloroform. The partition of cadmium chloride and iodide between water and amyl alcohol would seem to show that these salts are polymerised in alcohol, but more complex ions are probably formed in water. Acetic acid is bimolecular in chloroform and unimolecular in glycerol. The partition of boric acid between glycerol and amyl alcohol is in accordance with the fact that the acid forms an additive compound with glycerol. The principle of partition has only a limited application. E. W. W.

Deduction of the Stoichiometrical Laws. CARL BENEDICKS (*Zeit. anorg. Chem.*, 1906, 49, 284—296. Compare Ostwald, *Trans.*, 1904, 85, 506—522; Nasini, Abstr., 1905, ii, 514).—The paper contains a criticism of the views expressed by Ostwald in his Faraday Lecture, and is unsuitable for detailed abstraction.

The author agrees with Ostwald's view that it is not necessary to have recourse to the atomic theory to show the experimental necessity of the law of constant proportions, but considers that Ostwald's deduction of the law has more the character of a demonstration. The deduction of the law of combining weights from that of constant proportions is also regarded as faulty, since in one part of the proof the results of stoichiometrical experience have been drawn on. The author himself suggests another method of deducing the last-mentioned law which is free from the objection just referred to. G. S.

The Periodic System and the Methodical Classification of the Elements. GEORGE RUDOLF (*Chem. Zeit.*, 1906, 30, 595—596).—Polemical. A reply to Zengelis (compare this vol., ii, 276, 277). P. H.

Isomorphism and the Law of Mitscherlich. FRÉDÉRIC WALLERANT (*Ann. Chim. Phys.*, 1906, [viii], 8, 90—114).—A résumé of work already published (compare Abstr., 1904, ii, 31; 1905, ii, 151, 161, 237, 380). M. A. W.

Rapid Steam Generator. REISER (*Chem. Zeit.*, 1906, 30, 639).—In place of the ordinary wide metal can, the author employs a narrow one of not more than 5 cm. diameter, provided with a constant level adjustment to prevent its running dry. Owing to the small amount of water actually in the can it can be raised to the boiling point in a comparatively short time. P. H.

Gas Generator for Hydrogen Sulphide, Hydrogen, and other Gases. ALLEN P. FORD (*J. Amer. Chem. Soc.*, 1906, 28, 793—795).—A modified form of the apparatus described by Knorr (*Abstr.*, 1898, ii, 568). A safety funnel inserted in an aperture in the generating tower at the opposite side to the gas outlet prevents the water in the wash-bottle from being drawn back, and also affords facilities for washing out the apparatus without taking it to pieces. The arrangement is shown by means of a diagram. E. G.

Automatic Safety Siphon. RUDOLF L. STEINLEN (*Chem. Zeit.*, 1906, 30, 459).—The possibility of the entry of the liquid into the mouth of the operator engaged in starting the siphon is prevented by means of two valves. P. H.

Inorganic Chemistry.

Hydrogen Fluoride. III. ERNST DEUSSEN (*Zeit. anorg. Chem.*, 1906, 49, 297—300. Compare Abstr., 1905, ii, 311).—The constant boiling mixture of hydrogen fluoride and water contains 43·2 per cent. by weight of the acid, boils at 111° under 750 mm. pressure, and has the sp. gr. 1·138 at 18°. G. S.

Preparation of Pure Gases. HENRI MOISSAN (*Ann. Chim. Phys.*, 1906, [viii], 8, 74—83).—A *résumé* of work already published (compare Abstr., 1899, ii, 593 ; 1903, ii, 365, 642 ; 1905, ii, 26).

M. A. W.

Oxidations by Air. Problem of the Comparison of Velocities. ANDRÉ JOB (*Compt. rend.*, 1906, 142, 1413—1416. Compare Abstr., 1902, ii, 399 ; 1903, ii, 214).—A claim for priority (compare Fouard, this vol., i, 421). In order to obtain comparable results on the velocity of oxidation by air, it is essential that in the liquid under investigation the same concentration in oxygen should be maintained throughout the operation, that the temperature should be kept constant, and that a continuous record should be kept of the amount of oxygen absorbed. The author has devised apparatus which fulfils these conditions and is continuing the investigation. M. A. W.

Behaviour of Selenium in the Manufacture of Sulphuric Acid. SIGMUND LITTMANN (*Zeit. angew. Chem.*, 1906, 19, 1039—1044 and 1081—1089).—Selenium is met with during the manufacture of

sulphuric acid in a variety of forms; it occurs both as selenious acid and as elementary selenium produced by the reduction of selenium dioxide according to the equation $\text{SeO}_2 + 2\text{SO}_2 = \text{Se} + 2\text{SO}_3$; obtained in this way it may form either a gelatinous precipitate or a fine brick-red powder, according to the amount present. At temperatures above $80-90^\circ$, the red variety changes to a greyish-black modification, having a metallic lustre, whilst 0.03 per cent. is converted into a soluble form, which has not yet been identified. In addition to these, are the forms in which selenium occurs in solution either immediately preceding its precipitation or as a green solution in concentrated sulphuric acid. Selenic acid, H_2SeO_4 , is never found in the chamber process under normal conditions, which is in direct contradiction to Winteler's statement. The fact that the cooled gases from the pyrites burners yield the red variety and not the grey one, in spite of the fact that the temperature must have surpassed 100° , shows that it must have been formed from a gaseous compound which is capable of existing, at any rate for a short space of time, in contact with sulphur dioxide at a comparatively low temperature. The amount of selenium contained in the gas issuing from the pyrites burners was estimated by drawing several thousand litres of the gas through well-cooled wash-bottles containing glass wool moistened with hydrochloric acid; the selenium is thereby precipitated as a red powder which is then oxidised by means of nitric acid to selenious acid, in which form it is estimated by one of the known methods. The average amount of selenium in pyrites used in the author's experiments was 85 grams per ton, but 10 grams per ton suffice to make themselves visible to the naked eye in the various parts of the chamber process. The dark red sludge which is frequently observed in hot Glover acid contains about 2-4 per cent. of the total selenium in the pyrites. Quantitative experiments showed that incompletely denitrated Glover acid contained all its selenium in the form of selenium dioxide; dilute samples of Glover acid, on the other hand, contained a part of the selenium in some other form of combination in which it had the property of being precipitated from solution as a red powder by merely diluting the acid; in such cases the precipitation of red selenium on dilution could be prevented by drawing a feeble stream of nitric oxide through the acid immediately after it had been diluted. Inasmuch as only about 20 per cent. of the selenium from the pyrites could be accounted for in the Glover tower, it follows that the major portion must have passed on into the chambers; analysis of the chamber gases disclosed selenium solely, however, in the form of the dioxide. The tubes leading from the Glover tower to the chambers contained both red selenium and the combined form, but no dioxide. In regard to the influence of selenium on the colour of the concentrated acid, it was found that the green colour of the ordinary commercial acid was due to the presence of the compound SeSO_3 ; when this acid is further concentrated it becomes colourless owing to the conversion of this substance into the colourless SeO_2 .

From these observations it is concluded that wherever nitrosylsulphuric acid is formed or decomposed, either of the various forms of selenium is converted into selenious acid, and that the main quantity

of the selenium escaping from the pyrites exists in the form of a very volatile labile combination corresponding with a lower state of oxidation, such as SeO ; in this form it is readily reduced to elementary selenium or oxidised to selenium dioxide.

The following is recommended as a delicate test for selenium. The sulphuric acid containing selenious acid is diluted and treated with a crystal of potassium iodide; the iodine is then removed by adding an excess of sodium thiosulphate, when red selenium remains suspended in the solution, but rapidly changes to a lemon-yellow-coloured compound with sulphur. When the amount of selenium present is very small, it should be concentrated at the cathode by electrolysis and then oxidised with nitric acid before proceeding to test further. For quantitative determinations, the sulphuric acid should be first oxidised on the water-bath with concentrated nitric acid, when the selenium is oxidised to the dioxide; the oxides of nitrogen are then removed by drawing a rapid current of air through the hot solution, and the solution is treated with a slight excess of $N/10$ permanganate, the excess being then titrated back with $N/10$ oxalic acid. By this means the selenious oxide is quantitatively oxidised to the trioxide.

P. H.

Crystalline Form of Nitrogen Sulphide, N_4S_4 . ETTORE ARTINI (*Chem. Centr.*, 1906, i, 1774; from *Rend. Istit. Lombardo Sci. Lett. Milan*, [ii], 37, 864—869).—Nitrogen sulphide, prepared by the action of gaseous ammonia on a solution of sulphur chloride in benzene, and purified by fractional crystallisation from carbon disulphide, forms translucent, mostly tabular, orange, monoclinic crystals containing cavities and bubbles, but with flat, lustrous surfaces [$a:b:c = 0.8806:1:0.8430$; $\beta = 89^\circ 20'$].

E. W. W.

Electrochemical Problem of the Fixation of Nitrogen. PHILIPPE A. GUYE (*J. Soc. Chem. Ind.*, 1906, 25, 567—578).—In regard to the chemical action of the electric arc in atmospheric air, it is found that by employing a high temperature for the combustion of nitrogen, the yield of nitric oxide is increased and the transformation occurs more rapidly. Owing, however, to the tendency for the nitric oxide to be dissociated at high temperatures into nitrogen and oxygen, the success of the process depends on the rapid cooling of the oxide. This has been realised in practice by rapidly sweeping the gases out of the region of the electric arc, and more recently use has been made of mechanical devices by which arcs were successively lighted and interrupted several thousand times per second, or the arc has been forced to play in different regions of the space. The gases as they pass out of the arc chamber contain some 1 or 2 per cent. by volume of nitric oxide; by allowing the gas to cool to about 500° to 600° , the nitric oxide is converted into nitrogen trioxide and peroxide, which are then absorbed in water.

P. H.

Direct Synthesis of Nitric Acid and the Nitrates from their Elements at the Ordinary Temperature. MARCELLIN BERTHELOT (*Compt. rend.*, 1906, 142, 1367—1379).—Nitrogen and

oxygen combine in the presence of water or dilute alkalis, at the ordinary temperature, under the influence of a silent electrical discharge, to produce nitric acid according to the equation $2\text{N}_2 + 5\text{O}_2 + 2\text{H}_2\text{O} + \text{Aq.} = 4\text{HNO}_3$ dil.; neither nitrous acid nor ammonia are produced, and the reaction is independent of the relative proportions of the two gases present in the original mixture, and proceeds until nearly all the oxygen is absorbed. In one series of experiments, a mixture of oxygen and nitrogen in varying proportions was circulated through an ozone apparatus (*Ann. Chim. Phys.*, 1877, [v], 10, 166), and when atmospheric air was passed at the rate of half a litre per hour the amount of nitric acid formed at the end of eight hours was 0.154 gram, which represents a mean value of 0.0192 gram per hour from 3.6 c.c. of nitrogen and 12.6 c.c. of oxygen extracted from half a litre of air. Similar results were obtained in another series of experiments made under varying conditions of temperature ($8-80^\circ$) and pressure, the mixture of gases being enclosed in a sealed tube containing water or dilute alkali. The velocity of the reaction diminishes as the gaseous pressure diminishes; thus, in one experiment, when 0.038 gram of nitric acid was obtained in eight and a half hours from 27 c.c. of a mixture of gases in the proportion $2\text{N}_2 : 5\text{O}_2$, enclosed at atmospheric pressure in a vessel over dilute potassium hydroxide, during the first fifteen minutes the pressure fell to 0.68 m. and the rate of formation of acid was 0.16 mg. per minute, whilst the corresponding values for the last two hours were 0.04 m. and 0.016 mg. respectively.

M. A. W.

Phosphorus Chloronitride. ADOLPHE BESSON and GEORGES ROSSET (*Compt. rend.*, 1906, 143, 37—40. Compare Abstr., 1892, ii, 1152).—Phosphorus chloronitride, PCl_2N , is most readily obtained by heating equal quantities of phosphorus pentachloride and ammonium chloride and resubliming the washed and dried product under reduced pressure. It is practically insoluble in water, but dissolves in light petroleum, benzene, carbon tetrachloride, phosphorus oxychloride, sulphur dioxide, and nitrogen peroxide. If the chloronitride is placed in one of the arms of a Faraday tube and nitrogen peroxide in the other, the peroxide is quickly absorbed with the formation of a liquid which, on cooling, deposits long, needle-shaped crystals. These are stable in an atmosphere of nitrogen peroxide, but give off this gas very rapidly when removed from the tube.

Cryoscopic measurement of the molecular weight of the chloronitride in benzene solution gave 377, which corresponds approximately with the formula $(\text{PCl}_2\text{N})_3 = 348$. It is slowly decomposed by water at the ordinary temperature, rapidly at $150-200^\circ$ in a sealed tube; the reaction is represented by the equation $(\text{PCl}_2\text{N})_3 + 12\text{H}_2\text{O} = 3\text{NH}_3 + 3\text{H}_3\text{PO}_4 + 6\text{HCl}$. It is not acted on by ozone; with sulphur trioxide it reacts at the ordinary temperature, and at 150° complete decomposition takes place. When heated with nitrogen peroxide at $200-250^\circ$ in a sealed tube, nitrogen, nitrous and nitric oxides, chlorine, nitrosyl and nitroxyl chlorides, and a substance of the composition $2\text{P}_2\text{O}_5 \cdot \text{NO}_2$ are formed. This substance has been also obtained by heating phosphoric oxide with nitrogen peroxide at 200° in a sealed tube; it gives off

nitrogen peroxide when heated, and deliquesces in the air with loss of nitrogen peroxide. H. M. D.

Melting Points and Boiling Points of the Fluorides of Phosphorus Silicon and Boron. HENRI MOISSAN (*Ann. Chim. Phys.*, 1906, [viii], 8, 84—90).—A *résumé* of work already published (compare Abstr., 1904, ii, 331; 1905, ii, 26). M. A. W.

Non-existence of Phosphorus Trisulphide. R. BOULOUCH (*Compt. rend.*, 1906, 143, 41—44. Compare this vol., ii, 438).—The substance described as phosphorus trisulphide has no definite melting point, and when distilled fractionation takes place. When an intimate mixture of rhombic sulphur and the sulphide, P_4S_3 , is heated above 50° , the mass undergoes more or less complete liquefaction. If the temperature is raised to something above 100° , a reaction takes place which is accompanied by considerable development of heat and change in colour from yellow to red. When a mixture of the composition PS_2 , completely liquefied by heating at 100° , is maintained at this temperature for several days, a precipitate is formed the composition of which corresponds very closely with the formula P_3S_5 .

Liquids of composition varying from P_4S_3 to P_4S_8 when quickly cooled generally undergo partial solidification, and from the liquid and solid phases substances corresponding closely with the formulæ P_3S_5 and P_4S_8 respectively have been separated. The author's experiments indicate that the existence of a sulphide of phosphide intermediate between P_4S_3 and P_3S_5 is improbable.

H. M. D.

Action of Ammonia on Phosphorus Pentasulphide: Thiophosphates and Thiophosphoric Acids. ALFRED STOCK [with BERTHOLD HOFFMANN, F. MÜLLER, H. VON SCHÖNTHAN, and H. KÜCHLER] (*Ber.*, 1906, 39, 1967—2008. Compare Stock and Hoffmann, Abstr., 1903, ii, 207).—The phosphorus pentasulphide (Stock and Thiel, Abstr., 1905, ii, 703) was purified by solution in carbon disulphide; the liquid ammonia was dried with sodium and distilled.

Ammonium di-iminopentathiopyrophosphate (Stock and Hoffmann, *loc. cit.*) is very hygroscopic, and dissolves in cold water, forming a yellow solution which deposits sulphur and acquires an odour of ammonium sulphide; the freshly prepared aqueous solution does not give the reactions of phosphoric acid. The pyrophosphate decomposes when heated, forming an infusible, greyish-brown powder containing nitrogen and traces of sulphur.

The additive product, $P_2S_5 \cdot 7NH_3$, which is a mixture of ammonium iminotrithiophosphate and ammonium nitrilodithiophosphate, separates slowly in transparent crystals from the yellow solution formed by dissolving phosphorus pentasulphide in liquid ammonia.

Ammonium iminotrithiophosphate forms hygroscopic crystals, which lose ammonia and effloresce in dry air, is slightly soluble in liquid ammonia, and forms a strongly alkaline aqueous solution; this gives the reactions of ammonium trithiophosphate, but does not react with

sodium nitroprusside until after some time, when it has an odour of hydrogen sulphide. When ignited on platinum, the iminotrithiophosphate burns with a flame resembling that of sulphur, and yields a residue of impure phosphorus nitride. In a vacuum at 50° , or in a dessicator over sulphuric acid, the triammonium salt loses ammonia, forming *diammonium hydrogen iminotrithiophosphate*,

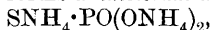


which, when heated at 100° in a vacuum, yields ammonia and *ammonium dihydrogen iminotrithiophosphate*, $\text{SNH}_4 \cdot \text{P}(\text{SH})_2 \cdot \text{NH}_3$. *Disodium hydrogen iminotrithiophosphate*, $\text{SH} \cdot \text{P}(\text{SNa})_2 \cdot \text{NH}_3$, is formed by the action of sodium ethoxide on the triammonium salt; it is decomposed by water, forming *disodium hydrogen dithiophosphate* and hydrogen sulphide.

Ammonium trithiophosphate, $\text{PO}(\text{SNH}_4)_3 \cdot \text{H}_2\text{O}$, prepared by the action of water on ammonium iminotrithiophosphate, loses H_2O slowly in a vacuum desiccator, forms ammonium dithiophosphate (Kubierschky, Abstr., 1885, 632) on further treatment with water, and yields in aqueous solution with zinc sulphate, cadmium sulphate, and manganese chloride, voluminous, white precipitates; with mercuric chloride and lead and bismuth nitrates, yellow or red precipitates which change into the black sulphides when boiled; with chromium and copper sulphates, green, slimy precipitates; and with ammoniacal silver solution, a rust-brown precipitate which rapidly becomes black. The lead and calcium salts have been obtained in a state of purity.

Light yellow *ammonium dithiometaphosphate*, $\text{PS}_2 \cdot \text{ONH}_4$, is formed by the action of hydrogen sulphide on ammonium trithiophosphate at 175° ; it is decomposed by water, forming hydrogen sulphide.

Ammonium dihydrogen thiophosphate, $\text{SNH}_4 \cdot \text{PO}(\text{OH})_2$ (compare Wurtz, *Ann. Chim. Phys.*, 1864, [iii], 20, 472), formed by the action of water on iminotrithiophosphoric acid, decomposes when heated, forming hydrogen sulphide and ammonium metaphosphate, and on treatment with ammonia forms *ammonium thiophosphate*,



which is obtained as a loose, white, crystalline powder. It loses 2NH_3 when gently heated or when dried over sulphuric acid in a vacuum, and gives precipitates with solutions of metallic salts, as does the sodium salt (Kubierschky, *loc. cit.*).

When heated in an atmosphere of hydrogen sulphide at 140 — 145° for twelve hours, and then at 175 — 180° for several days, ammonium iminotrithiophosphate forms ammonium hydrogen sulphide and *iminotrithiophosphoric acid*, $\text{NH} \cdot \text{P}(\text{SH})_3$, which is yellow, becomes darker when heated, has a sp. gr. 1.78 at 16.5° , is insoluble in carbon disulphide, and is readily decomposed by water, forming ammonium dihydrogen thiophosphate. The white *hydrochloride*, $\text{P}(\text{SH})_3 \cdot \text{NH}_4\text{Cl}$, loses hydrogen chloride at 125° and yields sulphur and hydrogen sulphide when treated with water. The acid, when strongly heated, loses hydrogen sulphide and forms *di-iminopentathiopyrophosphoric acid*, $\text{S}[\text{P}(\text{SH})_2 \cdot \text{NH}]_2$, which dissolves in liquid ammonia, forming a yellow solution, and gradually yielding colourless crystals.

When heated above 180° in a vacuum, ammonium iminotrithiophosphate yields white *thiophosphoric nitrile*, $\text{N} \cdot \text{P} \cdot \text{S}$ (compare Glatzel,

Abstr., 1893, ii, 458), which is hydrolysed slowly by boiling water, more quickly by dilute hydrochloric acid, forming phosphoric acid, hydrogen sulphide, and ammonia; it does not react with liquid ammonia at 100° , and is attacked by fuming nitric acid only when heated. It decomposes when strongly heated, forming phosphorus pentasulphide and phosphorus nitride. When heated in a vacuum at 200° , iminotrithiophosphoric acid forms an intermediate *product*, $S(PS:NH)_2$, which forms thiophosphoric nitrile at $250-280^{\circ}$.

When treated with anhydrous liquid hydrogen chloride, ammonium or lead trithiophosphate yields a *product*, which may be pentathio-pyrophosphoric acid, $H_4O_2S_5P_2$, or a mixture of thiophosphoric acids; it melts at -55° , forming a yellow oil, which is soluble in carbon disulphide, evolves hydrogen sulphide at the ordinary temperature, reacts energetically with water, depositing sulphur, and forms phosphorus pentasulphide when heated with carbon disulphide.

Silver tetrathio-phosphate (Glatzel, *loc. cit.*), which is obtained as a yellow, crystalline powder when finely divided silver chloride is heated with carbon disulphide and a slight excess of phosphorus pentasulphide at 200° , does not react with liquid hydrogen chloride.

The action of anhydrous hydrogen bromide on ammonium trithiophosphate leads to the formation of thiophosphoryl bromide and a small amount of a *dibromothio-acid*, $SH \cdot PBr_2 \cdot S$.

Thiophosphoryl bromide is obtained in a yield of 40 per cent. of the theoretical when phosphoryl bromide is dissolved in liquid hydrogen sulphide; the conversion of the oxybromide into the thio-bromide is complete in presence of a dehydrating agent.

Ammonium nitrilodithiophosphate (Stock and Hoffmann, *loc. cit.*) is obtained on evaporation of its solution in ammonia as a white, resinous mass, readily soluble in water; when heated at 100° in a vacuum, it loses NH_3 , forming *ammonium hydrogen nitrilodithiophosphate*, $SH \cdot P(SNH_2):N$, which is crystalline, white, and when exposed to moist air has an odour of hydrogen sulphide. At $180-200^{\circ}$, in a current of an indifferent gas or in a vacuum, the ammonium salt yields ammonia and hydrogen sulphide; at 300° , thiophosphoric nitrile, and at 850° , phosphorus nitride, are formed. Whilst free *nitrilodithiophosphoric acid*, $N:P(SH)_2$, is unstable in aqueous solution, being hydrolysed to phosphoric acid, ammonia, and hydrogen sulphide, the nitrile group is not hydrolysed when the salts are boiled with aqueous alkali hydroxides. When boiled with water alone or in presence of ammonia, or when treated with an ammoniacal solution of silver oxide at the ordinary temperature, the ammonium salt yields ammonium phosphate. The *lead*, *barium* ($+ H_2O$), and *sodium* nitrilodithiophosphates are described.

Yellow phosphorus and sulphur react in liquid ammonia at 100° , forming ammonium iminotrithiophosphate, which is formed also by the action of liquid ammonia on phosphorus trisulphide and hexasulphide.

G. Y.

Variations of State of Amorphous Carbon under the Influence of Rapid Variations of Temperature. O. MANVILLE (*Compt. rend.*, 1906, 142, 1523—1525. Compare this vol., ii, 439).—

When a sample of amorphous carbon, which originally united with oxygen at 87° , was heated in a vacuum at 450° and suddenly cooled, it was found to enter into combination with oxygen at 50° . On subjecting the carbon to temperature variations ranging between 15° and 350° , the temperature of oxidation remained practically constant at 50° . When heated again at 450° and slowly cooled, the condition of the carbon was altered and the temperature of oxidation was now found to change considerably with the variations of temperature to which the carbon was submitted.

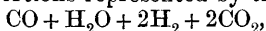
Similar experiments with a sample of carbon, which oxidised originally at 245° , showed that the invariable condition, corresponding in this case with an oxidation temperature of 115° , was unchanged by six oscillations of the temperature between 15° and 135° , but after twenty such oscillations a new invariable condition, corresponding with an oxidation temperature of 154° , was found to have set in. This invariability disappeared as in the first case, when the carbon was heated at 450° and slowly cooled.

H. M. D.

Solubility of Carbon in Calcium Carbide. H. MOREL KAHN (*Compt. rend.*, 1906, 143, 49—51).—Commercial calcium carbide always contains a certain amount of graphite which is supposed to have separated from solution in the fused carbide on cooling. The author finds that the amount of carbon dissolved by the fused carbide increases with the intensity of the current employed in the furnace and also with the time of passage of the current when its intensity is kept constant. In an experiment in which a current of 500—600 amperes was passed for six and a half minutes, five per cent. of carbon was taken up by the fused carbide. When the period of heating is further prolonged, the results are complicated by decomposition of the carbide.

H. M. D.

Action of Carbon Monoxide at a Red Heat on Water-Vapour, and of Hydrogen on Carbon Dioxide. Application of these Reactions to the Study of Volcanic Phenomena. ARMAND GAUTIER (*Compt. rend.*, 1906, 142, 1382—1387).—Carbon monoxide exerts a reducing action on water-vapour at 1200 — 1250° (compare Maquenne, *Abstr.*, 1883, 860). The reaction is a balanced one, and equilibrium is reached when the volume of hydrogen produced is double that of the carbon monoxide present as represented by the equation $3\text{CO} + 2\text{H}_2\text{O} = 2\text{CO}_2 + 2\text{H}_2 + \text{CO}$, and at the same time traces of formic acid are formed. The inverse action, namely, the reduction of carbon dioxide by hydrogen, proceeds readily at 1300° when the two dried gases are passed through a heated porcelain tube, and equilibrium is reached when the volume of carbon monoxide formed is half that of the hydrogen present, according to the equation $\text{CO}_2 + 3\text{H}_2 = \text{CO} + \text{H}_2\text{O} + 2\text{H}_2$. From the two equations given above it follows that mixtures of water vapour, carbon dioxide, carbon monoxide, and hydrogen are in equilibrium at a red heat when they are present in the proportions represented by the system



and these facts explain the presence of the oxides of carbon, water

vapour, and hydrogen in volcanic gases, and of formic acid in the gases and water. M. A. W.

Chemical Behaviour of Argon and Helium. W. TERNENT COOKE (*Zeit. physikal. Chem.*, 1906, 55, 537—546).—The author has determined the vapour density of zinc, cadmium, mercury, sulphur, selenium, and arsenic in atmospheres of argon and helium; the vapour densities of most of these elements have been determined also in atmospheres of nitrogen and hydrogen for the sake of comparison. Since the density of zinc in argon is 12 per cent. higher than in nitrogen, it may be concluded that zinc and argon have a distinct tendency to form a compound. This tendency is found to exist also in the case of cadmium and helium, mercury and argon, mercury and helium, selenium and argon (slight), selenium and helium (slight).

J. C. P.

Behaviour of Helium in a Platinum-iridium Vessel at High Temperatures. ERNST DORN [with F. CARIO] (*Chem. Centr.*, 1906, i, 1645; from *Physikal. Zeit.*, 7, 312).—When helium was heated in a strong platinum-iridium vessel for thirty to sixty minutes at 640—1420°, the pressure remained absolutely constant. E. W. W.

Action of Oxygen on Rubidium-ammonium. ÉTIENNE RENGADE (*Compt. rend.*, 1906, 142, 1533—1534).—When a solution of rubidium in liquid ammonia is oxidised, the blue colour disappears, and a pinkish-white, voluminous precipitate of the composition Rb_2O_2 separates. The suspended oxide absorbs a further quantity of oxygen and a yellow oxide, Rb_2O_4 , is formed. In the case of potassium and caesium, an intermediate trioxide is also formed, but there is no evidence of the formation of the corresponding rubidium compound. In the experiments the oxidation should be effected rapidly, since the rubidium dioxide tends to react with the metal-ammonium compound according to the equations $\text{Rb}_2\text{O}_2 + 2\text{RbNH}_3 = 2\text{RbOH} + 2\text{RbNH}_2$, $\text{Rb}_2\text{O}_2 + \text{RbNH}_2 = 2\text{RbOH} + \text{Rb} + \text{N}$.

H. M. D.

Caesium Chromates. FRANK R. FRAPRIE (*Zeit. Kryst. Min.*, 1906, 42, 113—119).—The following salts were prepared and described in detail crystallographically: caesium chromate, Cs_2CrO_4 , in two modifications (rhombohedral and orthorhombic); caesium dichromate, $\text{Cs}_2\text{Cr}_2\text{O}_7$ (anorthic); and caesium trichromate, $\text{Cs}_2\text{Cr}_3\text{O}_{10}$ (rhombohedral).

L. J. S.

Silver-magnesium Alloys. S. F. SCHEMTSCHUSCHNY (*Zeit. anorg. Chem.*, 1906, 49, 400—414. Compare Parkinson, *Trans.*, 1897, 67, 117).—The freezing-point curve of the system shows a distinct maximum at 820° and 50 atom. per cent. silver, corresponding with the composition of the compound MgAg , a transition point for the compound Mg_3Ag at 492° and 22·57 atom. per cent. silver, and two eutectic points at 469° and 17·3 atom. per cent., and 756° and 65·9 atom. per cent. of silver respectively. The composition of the compound Mg_3Ag , which decomposes below its melting point, has been determined by the

methods described in Tammann's recent papers. The compound $MgAg$ forms mixed crystals with magnesium from 34.57 to 50 atom. per cent. of silver, and with silver from 50 to 62 atom. per cent. of the same metal. Magnesium also forms solid solutions with silver which are saturated when 28.15 atom. per cent. of the former metal is present; the freezing-point depression of silver due to the presence of zinc is therefore much smaller than the theoretical value.

The alloys of silver and magnesium are harder than the component elements, and the brittleness reaches its maximum at points corresponding with the composition of the compounds. Those rich in magnesium are easily oxidised, decompose water more readily than magnesium, and yield a black powder on long exposure to air. The fresh surface of alloys containing from 57 to 70 atom. per cent. of magnesium is yellowish in colour.

The paper is illustrated with ten micro-photographs.

G. S.

Structure of Electrolytic Calcium. L. DOERMER (*Zeit. anorg. Chem.*, 1906, 49, 362—364).—A freshly fractured surface of metallic calcium from the electro-chemical works at Bitterfeld showed small aggregates of the appearance of ice crystals embedded in the main bulk of metal. These aggregates are more readily acted on by moisture and less affected by hydrochloric acid in absolute alcohol than the ground mass; they are not observable in specimens of the metal which have been melted and allowed to resolidify. The author considers that these differences are brought about by traces of impurities in the technical product.

G. S.

Attempts to prepare Sub-salts of Calcium. ANTOINE GUNTZ and HENRY BASSETT, jun. (*Bull. Soc. chim.*, 1906, [iii], 35, 404—418. Compare Moissan, Abstr., 1900, ii, 76; Borchers and Stockem, Abstr., 1903, ii, 19, and Guntz, Abstr., 1905, ii, 87).—Mixtures of metallic calcium with (1) calcium chloride, (2) calcium iodide, or (3) calcium fluoride were heated in various ways under reduced pressure or in presence of hydrogen, methane, or argon, and also in an iron crucible. The products obtained were similar to those secured by previous workers (*loc. cit.*), and usually assumed to be sub-salts of calcium. The authors are, however, of opinion that these indefinite products consist merely of mixtures of the unaltered salt with varying small proportions of calcium oxide and hydride, and that the property of liberating hydrogen from water shown by these products is due to calcium hydride, and not to calcium sub-salts as has been supposed. The hydride is formed, in the absence of free hydrogen, by the action of small quantities of water on the calcium, the hydrogen liberated subsequently combining with some of the residual metal.

T. A. H.

Action of Alkali Bromides on Barium Carbonate. EDM. TAPONIER (*Bull. Soc. chim.*, 1906, [iii], 35, 280—293).—The experiments were carried out on the same lines as those described by Cantoni and Goguélia (Abstr., 1905, ii, 87). The results show that the action of a solution of potassium or sodium bromide on barium carbonate,

suspended in water, increases with increase of time or concentration and with rise of temperature, and that in general the action of sodium bromide is more marked than that of potassium bromide. Potassium chloride, in all circumstances, is more active than potassium bromide, but this difference in activity is less marked in the case of the two corresponding sodium salts. The amount of barium carbonate decomposed by a boiling solution of ammonium bromide augments as the time of action is prolonged and the concentration of the bromide is increased.

At atmospheric temperature, and acting for a period of ninety-eight days, ammonium bromide exerts most and potassium bromide least action of the three salts used. Figures and curves illustrating these results are given in the original.

T. A. H.

Revision of the Atomic Weight of Cadmium. II. GREGORY P. BAXTER, MURRAY A. HINES, and HARRY L. FREVERT (*J. Amer. Chem. Soc.*, 1906, 28, 770—786. Compare Baxter and Hines, *Abstr.*, 1905, ii, 321).—The atomic weight of cadmium has been redetermined by the analysis of highly purified cadmium bromide. Weighed portions of the bromide, after fusion in a mixture of dry nitrogen and hydrogen bromide, were titrated against weighed portions of pure silver. The precipitated silver bromide was afterwards collected and weighed. Various corrections were applied to ensure the greatest possible accuracy. In this way the atomic weight of cadmium calculated from the ratio $\text{CdBr}_2 : 2\text{Ag}$ was found, as the average of seven analyses, to be 112.470, and from the ratio $\text{CdBr}_2 : 2\text{AgBr}$, 112.464, also as the average of seven analyses [$\text{Ag} = 107.930$, $\text{Br} = 79.955$]. Hence, as the average of both series, the atomic weight of cadmium was found to be 112.467, a value which is identical with that previously obtained from the analysis of the chloride. From the same analyses, the ratio $\text{Ag} : \text{Br}$ was found to be 57.4437.

It was found, as has been previously shown by Bailey and Fowler (*Trans.*, 1888, 53, 755), that phosphoric oxide is attacked by hydrogen chloride and is therefore unsuitable for drying the gas. It is shown, however, that no appreciable error is introduced from this source when a dry salt is fused in a current of hydrogen chloride which has been dried in this way. It is also found that when hydrogen bromide diluted with twice its volume of nitrogen is passed over phosphoric oxide no such effect is produced.

E. G.

Lead and Silver. K. FRIEDRICH [and PUCHTA] (*Metallurgie*, 1906, 3, 396—406).—A redetermination of the freezing-point curve of the lead-silver alloys has confirmed entirely the results of Heycock and Neville (*Abstr.*, 1897, ii, 245). The eutectic line can be traced almost to the limits of the diagram. The metals thus separate in a pure state, and no compounds are formed. The separation of lead and silver by crystallisation proceeds in exactly the same way in iron and in porcelain vessels; the suggestion of Bock (*Chem. Zeit.*, 1905, 29, 1199) that iron plays a part in the Pattison process for the desilverisation of lead is therefore unfounded. The position of the eutectic point is not displaced, and the form of the freezing-point curve is unaltered when

the fusions are carried out under a pressure of 5 atmospheres. Experiments with a specially constructed electric furnace provided with tap-holes at different levels showed that no segregation of the alloys takes place in the molten state.

C. H. D.

Lead Oxychlorides. RUDOLF RUER (*Zeit. anorg. Chem.*, 1906, 49, 365—383).—The freezing-point curve of mixtures of lead oxide and lead chloride up to 88 per cent. of the oxide has been plotted from the results of measurements made in platinum vessels in the usual way; larger proportions of oxide could not be employed owing to the destructive action on the platinum at the high temperatures necessary to effect fusion. The curve shows two maxima at 693° and 62 per cent. and 711° and 76 per cent. by weight of lead oxide, corresponding with the composition of the compounds $\text{PbCl}_2 \cdot 2\text{PbO}$ and $\text{PbCl}_2 \cdot 4\text{PbO}$ respectively; three eutectic points at 438° and 20 per cent., 691° and 64 per cent., and 703° and 82 per cent. of lead oxide respectively, as well as a break in the curve at 524° and 36 per cent. of the oxide. The latter arises from the fact that the compound, $\text{PbCl}_2 \cdot 2\text{PbO}$, which separates primarily from mixtures containing 47—62 per cent. by weight of lead oxide, reacts below 524° with the fused mass to form a third compound, $\text{PbCl}_2 \cdot \text{PbO}$, the formula of which has been established by thermal analysis. Between 68 and 78 per cent. of lead oxide, the compound $\text{PbCl}_2 \cdot 4\text{PbO}$ forms mixed crystals with $\text{PbCl}_2 \cdot 2\text{PbO}$ and PbO respectively. Lead chloride melts at 500°, the oxide at about 835°. There is no evidence of the existence of other compounds than the three just mentioned, although several others are referred to in the literature.

The compound $\text{PbCl}_2 \cdot \text{PbO}$ forms long, colourless needles, and occurs in nature as matlockite; $\text{PbCl}_2 \cdot 2\text{PbO}$ forms long, lustrous needles, and occurs naturally as mendipite, whilst $\text{PbCl}_2 \cdot 4\text{PbO}$ forms lustrous, yellow plates.

The paper is illustrated with eight microphotographs.

G. S.

Iodides of Thallium; their Limits of Existence and Valency. A Case of Inorganic Tautomerism. W. MAITLAND and RICHARD ABEGG (*Zeit. anorg. Chem.*, 1906, 49, 341—355. Compare Spencer and Abegg, *Abstr.*, 1905, ii, 369; Maitland, this vol., ii, 328).—The solutions obtained when thallous iodide, iodine, and iodine ions are brought together contain the ions I' , I_3' , TI' , TI''' , TII_4' , and the neutral molecules TH , TII_3 , and I_2 in equilibrium with the solid substances TH , TI_6I_8 , THI_3 , and I_2 . By a combination of solubility and partition measurements with potential observations, the concentrations of these neutral molecules and ions have been determined under different conditions and are given in tabular form.

Practically all the thallium in solution is present as the complex ion THI_4' ; the equilibrium constant $k = \text{THI}_4' / (\text{TI}''') \cdot (\text{J}')^4$ has the value $1.95 \cdot 10^{80}$. The calculation of this constant was rendered possible by previous determinations of the concentration ratios $\text{TI}''':\text{TI}'$ and $\text{I}_2:\text{I}'$ from the results of potential measurements (compare Spencer and Abegg; Maitland, *loc. cit.*); the absolute concentrations were sub-

sequently obtained from the solubility product of thallous iodide and the concentration of free iodine respectively.

The composition of the higher iodides, Tl_6I_8 and TlI_3 (already described by Jørgensen, this Journal, 1873, 475), was determined by shaking thallous iodide with solutions of iodine in carbon disulphide or carbon tetrachloride of different concentrations, as well as with solutions of the same element in aqueous potassium iodide, and it was found that the transition $\text{TlI} \rightarrow \text{Tl}_6\text{I}_8$ takes place at an iodine concentration of $0.76 \cdot 10^{-5}$ gram-molecules per litre of water, that of $\text{Tl}_6\text{I}_8 \rightarrow \text{TlI}_3$ at $3.3 \cdot 10^{-4}$ gram-molecules of iodine per litre. The higher iodides are not appreciably soluble in water or in the ordinary organic solvents.

The compound TlI_3 may be regarded as a tautomeric substance, since it reacts towards a solution either as a compound of univalent thallium with the I_3' ion or as an iodide of trivalent thallium depending on the substances with which it is brought into contact. From its solubility relations and the fact that a change in the composition of the solid substances in equilibrium with the solution produces only a relatively small change in the thallous iodide concentration, it follows that solid TlI_3 is to be regarded as essentially a thallous compound; this is in agreement with the fact of its isomorphism with rubidium and caesium tri-iodides. G. S.

Copper-cadmium Alloys. R. SAHMEN (*Zeit. anorg. Chem.*, 1906, 49, 301—310. Compare Mylius and Fromm, *Abstr.*, 1894, ii, 235; Heycock and Neville, *Trans.*, 1892, 61, 898).—From the results of an investigation of this system by Tammann's thermal method, controlled by microscopic observations, the author has obtained evidence of the existence of two compounds of copper and cadmium, the probable formulæ of which are Cu_2Cd and Cu_2Cd_3 .

The freezing-point curve shows a break at 42 atom. per cent. cadmium, a flat maximum at 564° and 59.4 atom. per cent. of the same metal, and two eutectic points at 542° and 45.4 atom. per cent. and 314° and 98 atom. per cent. of cadmium respectively. The components of the first eutectic mixture are the compounds Cu_2Cd and Cu_2Cd_3 ; of the second, Cu_2Cd_3 and cadmium. When the temperature falls to 552° in mixtures containing 0—42 atom. per cent. cadmium, the copper which at first separates enters into reaction with the fused mass with formation of the compound Cu_2Cd ; it was, however, found impossible to complete the reaction even by long heating, so that the composition of the compound could not be determined quite conclusively. Between 45.4 and 60 atom. per cent. and 60—98 atom. per cent. cadmium, the compound Cu_2Cd_3 forms mixed crystals with Cu_2Cd and cadmium respectively.

The alloys rich in cadmium are soft. With increase of copper they become harder and more brittle, until the alloy with the highest melting point is reached, beyond which point the brittleness gradually decreases.

Alloys containing 100—40 atom. per cent. of cadmium are steel-grey in colour; beyond the latter point, the yellowish-red colour becomes more pronounced as the proportion of copper increases. G. S.

Preparation of Oxychlorides of Mercury. M. DUKELSKI (*Zeit. anorg. Chem.*, 1906, **49**, 336—337. Compare Schoch, *Abstr.*, 1903, ii, 428).—The author has obtained two modifications of the compound $4\text{HgO}, \text{HgCl}_2$ by interaction of mercuric chloride and borax in aqueous solution; one was obtained from boiling concentrated solutions, and occurs in small, deep brown needles, the other separated from boiling dilute solutions in lustrous, golden-yellow scales. The question as to the identity of either of these compounds with one of the three modifications of the same oxychloride described by Schoch (*loc. cit.*) remains undecided. G. S.

Isomorphism of Mercuric Iodide with Zinc and Cadmium Iodide. ANDRÉ DUBOIN (*Compt. rend.*, 1906, **142**, 40—41).—Examination of the crystals which are successively deposited from solutions containing zinc or cadmium iodide together with mercuric iodide has shown that the latter forms a complete series of mixed crystals with the two former. The double iodides previously described, $\text{ZnI}_2, \text{HgI}_2$, $\text{CdI}_2, \text{HgI}_2$, and $\text{CdI}_2, 3\text{HgI}_2$, are in all probability isomorphous mixtures and not definite compounds. A solution saturated at 14.5° with regard to zinc and mercuric iodide has the composition $\text{HgI}_2, 1.87\text{ZnI}_2, 16.33\text{H}_2\text{O}$, and has the sp. gr. 2.82. H. M. D.

Magnesium and Manganese Mercury Iodides. ANDRÉ DUBOIN (*Compt. rend.*, 1906, **142**, 1338—1339. Compare *Abstr.*, 1905, ii, 637; this vol., ii, 85, 231, 286, 359).—The two crystalline double salts, $\text{MgI}_2, 2\text{HgI}_2, 7\text{H}_2\text{O}$, sp. gr. 3.8 at 0° , and $\text{MgI}_2, \text{HgI}_2, 9\text{H}_2\text{O}$, sp. gr. 2.9, are consecutively deposited from a saturated solution of magnesium and mercuric iodides having a sp. gr. 2.92 at 17.8° , and the composition represented by the formula $\text{MgI}_2, 1.29\text{HgI}_2, 11.06\text{H}_2\text{O}$.

Manganese mercury iodide, $3\text{MnI}_2, 5\text{HgI}_2, 20\text{H}_2\text{O}$, sp. gr. 3.8, is deposited when a saturated solution of manganese and mercuric iodides, having a sp. gr. 2.98 at 17° , is evaporated in the presence of sulphuric acid.

These double salts closely resemble the corresponding compound of calcium in their solubilities. M. A. W.

Aluminium-bismuth and Aluminium-tin Alloys. ALFRED G. C. GWYER (*Zeit. anorg. Chem.*, 1906, **49**, 311—319. Compare Heycock and Neville, *Trans.*, 1890, **57**, 376; Campbell and Matthews, *Abstr.*, 1902, ii, 399; Shepherd, *Abstr.*, 1904, ii, 486).—The melting-point curve of alloys of aluminium and tin falls regularly from the melting point of the former metal to the eutectic point of the alloy rich in tin; according to Heycock and Neville, the latter point lies at 229° , 3° below the melting point of tin, and the mixture contains 0.48 per cent. by weight of aluminium. The shape of the curve is not modified by heating the alloy for five hours at 710 — 720° , so that the metals do not enter into chemical combination. The results are in complete accord with the recent observations of Shepherd, but not with those of Campbell and Matthews (*loc. cit.*); the difference is probably due to the fact that the latter observers did not stir the alloys while cooling.

Aluminium and bismuth show only a small mutual solubility. The

saturated solution of bismuth in aluminium contains about 0.5 atom. per cent. of the former metal and solidifies at 652° , about 5° below the melting point of aluminium. At the same temperature, the layer rich in bismuth contains about 8 atom. per cent. of aluminium, but the solubility diminishes with decrease of temperature, and is practically zero at the melting point of bismuth. The two metals show no sign of chemical combination, even on heating for some time at 1200° (compare Tamman, this vol., ii, 88). G. S.

Knapp's Boron-ultramarine. JOSEF HOFFMANN (*Zeit. angew. Chem.*, 1906, 19, 1089—1095).—The author has studied the origin of the blue colour first observed by Knapp (*Dingler's Polyt. J.*, 1879, 233, 479) in connection with his investigations on boron glass. Dark blue boron-ultramarine is best obtained by fusing together 3.6 parts of borax, 1.5 parts of boric acid, and 0.9 part of sodium sulphide; if less boric acid or more sulphide is used, the resulting glass is either green or brown, but the blue colour can be easily restored by the addition of more boric acid. Sulphur or the sulphides of calcium, barium, strontium, or potassium may be substituted for sodium sulphide. A similar blue mass may also be obtained by fusing together 17 grams of boron trioxide and 2 grams of sodium sulphide, but no blue colour was obtained by fusing either boric acid or borax with sulphur alone. The yellow mass obtained by heating borax with sulphur was turned blue by the addition of phosphoric oxide, alum, hydrochloric or sulphuric acid; excess of the latter acid causes the blue colour to disappear again. The blue mass obtained by either of the above processes becomes colourless when strongly heated. Similar blue glasses may be obtained by heating microcosmic salt with sodium sulphide or sulphur and boric acid.

Blue boron-ultramarine has a hardness of 5, and is slightly soluble in water to form a colourless alkaline solution; it dissolves in cold hydrochloric acid, the solution on warming evolving hydrogen sulphide. The blue mass when heated until it becomes colourless no longer contains sulphur. Similar blue compounds can also be obtained by exposing a mixture of borax and boron trioxide to a stream of hydrogen sulphide or of carbon disulphide and subsequently heating. The lowest proportion of boron trioxide which yields a blue compound corresponds with the formation of a triborate of the type $\text{Na}_2\text{O}, 3\text{B}_2\text{O}_3$. P. H.

Crystallography of Iron. FLORIS OSMOND and G. CARTAUD (*Compt. rend.*, 1906, 142, 1530—1532; 143, 44—46).—The three varieties of iron, α -, β -, and γ -ferrite, crystallise in the cubic system. With the object of ascertaining whether structural differences are exhibited by the three allotropic forms, the authors have examined the pressure figures and the position of the twins produced mechanically and also by deformation followed by annealing. The pressure figures of γ -iron consist entirely of straight lines, whilst β -iron gives rise to curved lines and α -iron to both, although the curved lines predominate. In the case of the α -form, mechanical twinning of the fluorite type takes place; after deformation and annealing there is no twinning.

The β -form does not yield twins by either process, whilst the γ -form exhibits the phenomenon in both cases.

When ordinary manganese steel is heated at 1100° and hardened by plunging into cold water, the martensite structure is recognisable under the microscope. This structure is characteristic of γ -iron, but when very rapid cooling takes place the martensite structure is retained even when the γ -iron has undergone complete transformation into the α -modification. Meteoric irons show the martensite structure although the iron exists in the α -form. The reason for this is the lowering of the transition temperature to such an extent by the nickel present that the iron cannot assume the characteristic structure of the α -form. Such a condition may always be expected when an allotropic change accompanied by alteration of volume takes place in the solid state if the mechanical stress set up is capable of bringing about mechanical twinning.

H. M. D.

Determination of the Transition Points of Steels by the Electrical Resistance Method. P. FOURNEL (*Compt. rend.*, 1906, 143, 46—49).—The material, in the form of wires 0.3 mm. in diameter and 30 cm. long, was heated in a vacuum by means of an electrical resistance furnace and the resistance measured by the potentiometer method. Curves representing the relationship between the electrical resistance and the temperature are drawn for five samples of steel. The transition points designated by Osmond A_1 , A_2 , and A_3 are clearly indicated by breaks in the curves in the case of the steels containing a small amount of carbon. The composition of the steels and the critical temperatures are given in the table:

Percentage of C.	Si.	Mn.	A_1 .	A_2 .	A_3 .
0.08	0.24	0.43	—	775°	880°
0.11	0.02	0.35	670°	780	890
0.22	0.33	0.57	695	740	790
0.37	0.126	0.47	$730-770^\circ$ $730-750$		
1.05	?	0.25			

H. M. D.

Copper Steels. PIERRE BREUIL (*Compt. rend.*, 1906, 142, 1421—1424).—Two series of copper steels were prepared, one containing 0.168 to 0.150 per cent. of carbon, the other 0.336 to 0.282 per cent.; in each series the copper varied from 0.0 to 32 per cent., and each steel contained 0.10 to 0.15 per cent. of manganese, 0.220 per cent. of silicon, 0.020 per cent. of phosphorus, and 0.015 per cent. of sulphur. The members of the first series and those of the second up to and including the one containing 16 per cent. of copper formed homogeneous ingots, but no steel could be prepared containing 0.282 per cent. of carbon and 32 per cent. of copper. The ingot divided into two parts: the upper part contained 34.2 per cent. of copper at the core and 21.2 per cent. at the surface, whilst the corresponding numbers for the lower part were 74.8 and 24.4 respectively. The copper steels not containing more than 4 per cent. of copper are without colour and can be rolled, the steels of higher copper content have a red colour and are

too brittle to be worked. All the steels are magnetic, and their hardness, determined by Brinell's method, increases with the amount of copper, and the cooling curves obtained by Osmond's method show a large number of singular points. M. A. W.

Artificial Crystals of Ferric Hydroxide and of Anhydrous Ferric Oxide Pseudomorphous with Ferric Sulphate. ALBERT VESTERBERG (*Ber.*, 1906, **39**, 2270—2274).—Iron powder (*ferrum redactum*) is added to hot dilute sulphuric acid (1 : 1) and the mixture heated until the acid begins to fume and the iron is transformed into a faintly-red, crystalline powder of ferric sulphate. The acid is poured off as completely as possible and the crystals, without being washed, are placed in water and shaken with a solution of sodium hydroxide (1 : 2). The copper-coloured, crystalline meal is finally washed with hot water and dried at the ordinary temperature. The substance forms six- or eight-sided, isotropic plates, has a yellowish-brown or reddish-brown colour, is very friable, has a sp. gr. 3·234 at 15°, and is easily soluble in 20 per cent. hydrochloric acid. The composition corresponds approximately with the formula $\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, but small quantities of sodium, silicon, and manganese are also present in the substance, which is pseudomorphous with ferric sulphate. When dried in a desiccator, the substance changes into a monohydrate, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, which is not very stable, and begins to lose water at 100°, but differs from Brunck and Graebe's monohydrate (*Abstr.*, 1881, 126; van Bemmelen and Klobbie, *Abstr.*, 1903, ii, 169) in being very hygroscopic and in being pseudomorphous with anhydrous ferric sulphate.

The anhydrous ferric oxide resembles the hydrated form in appearance, but is redder and has a sp. gr. 5·06. C. S.

The System: Iron and Sulphur. WILHELM TREITSCHKE and GUSTAV TAMMANN (*Zeit. anorg. Chem.*, 1906, **49**, 320—335. Compare Le Chatelier and Ziegler, *Bull. Soc. Encouragement Ind.*, 1902, p. 368).—Ferrous sulphide and iron are not completely miscible in the fused condition, mixtures containing 8—80 per cent. of ferrous sulphide separating into two layers at 1400°. The freezing-point curve falls from 1540°, the freezing-point of iron, to 1400°, remains horizontal until the disappearance of the layer rich in iron, then falls to the eutectic temperature, 970°, and finally rises to 1300°, the freezing point of ferrous sulphide. The eutectic mixture contains about 16 per cent. of the sulphide. The components separate to a great extent in the form of two saturated mixed crystals, containing 3 and 96 per cent. by weight of iron respectively.

After crystallisation is complete, secondary changes due to polymorphous transformations of the components take place. Pure iron shows two transition points at 855° and 760°, corresponding with the transformation of γ - to β -iron and β - to α -iron respectively; the first of these is lowered to a greater extent than the second by the presence of ferrous sulphide, and with less than 92 per cent. of iron there is only one break in the cooling curve at 800°, which is probably connected with the solubility of ferrous sulphide in γ -iron. There is some evidence to show that when the temperature of mixtures rich in iron falls to

about 800° , the mixed crystals undergo partial separation into their components. At 130° occurs the transition of βFeS to αFeS , already observed by Le Chatelier and Ziegler; it is attended by considerable dilatation.

The deleterious effect of traces of sulphur on the properties of iron is discussed in the light of the above results. In mixtures containing more than 2 per cent. of sulphur, this effect is due to the presence of a readily fusible layer of sulphide between the particles of iron. That the presence of even 0.02 per cent. of sulphur is disadvantageous is to be ascribed to the brittle character of the mixed crystals rich in iron.

The paper is illustrated with microphotographs.

G. S.

Action of Water Vapour on Sulphides at a Red Heat. Production of Free Metals. Application to Volcanic Phenomena. ARMAND GAUTIER (*Compt. rend.*, 1906, 142, 1465—1470).—At an incipient red heat the sulphides of iron are decomposed by water vapour according to the equation $3\text{FeS} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 3\text{H}_2\text{S} + \text{H}_2$; at a higher temperature, sulphur dioxide and sulphur are also formed. When heated to bright redness in a current of water vapour, lead sulphide decomposes according to the equations $3\text{PbS} + 2\text{H}_2\text{O} = 3\text{Pb} + 2\text{H}_2\text{S} + \text{SO}_2$, $2\text{H}_2\text{S} + \text{SO}_2 = 2\text{H}_2\text{O} + 3\text{S}$. Sulphur dioxide is evolved in small quantity, and free sulphur mixed with a little lead sulphate collects in the cool part of the tube. The sulphate is probably formed by the reaction $\text{PbS} + 2\text{SO}_2 = \text{PbSO}_4 + 2\text{S}$. In a similar manner, cuprous sulphide is decomposed at a white heat according to the equation $\text{Cu}_2\text{S} + 2\text{H}_2\text{O} = 2\text{Cu} + \text{SO}_2 + 2\text{H}_2$. The free metals are thus obtained in the case of the feebly electropositive metals lead and copper.

On passing a current of hydrogen sulphide, saturated with water vapour at 100° , through a red-hot tube provided with a condenser, sulphurous acid, sulphuric acid in small quantity, and colloidal and precipitated sulphur collect in the latter, and hydrogen is also evolved. The presence of sulphur dioxide in volcanic gases can thus be easily explained by the displacement and oxidation of the sulphur of metallic sulphides by the action of water vapour at high temperatures.

H. M. D.

Action of Hydrogen Sulphide on Certain Oxides. Application to Volcanic Phenomena and Thermal Springs. ARMAND GAUTIER (*Compt. rend.*, 1906, 143, 7—12. Compare preceding abstract).—Magnetic oxide of iron is transformed by hydrogen sulphide at a white-red heat into ferrous sulphide with evolution of hydrogen, sulphur dioxide, and a small quantity of sulphur trioxide. The reaction in the case of ferric oxide is similar and corresponds with the equation $2\text{Fe}_2\text{O}_3 + 7\text{H}_2\text{S} = 4\text{FeS} + 3\text{SO}_2 + 7\text{H}_2$. Alumina is converted into the oxysulphide according to the equation $4\text{Al}_2\text{O}_3 + 9\text{H}_2\text{S} = 2\text{Al}_2\text{O}_3 \cdot \text{Al}_2\text{S}_3 + 3\text{SO}_2 + 9\text{H}_2$; silica gives the oxysulphide, $\text{SiO}_2 \cdot \text{SiS}_2$, and aluminium silicates are also partially decomposed in a similar manner.

The products obtained by passing a mixture of carbon dioxide and hydrogen sulphide through a porcelain tube at a white-red heat are water, carbonic oxide, carbon oxysulphide, and hydrogen. The relative

amount of the oxysulphide formed is not appreciably altered by varying the proportions of the carbon dioxide and hydrogen sulphide in the entering gas mixture. The reaction is represented by the equation $8\text{CO}_2 + 9\text{H}_2\text{S} = 3\text{COS} + 5\text{CO} + \text{H}_2 + 8\text{H}_2\text{O} + 6\text{S}$. The fact is recalled that carbon oxysulphide has been found by several observers in volcanic gases and also in sulphuretted waters in volcanic neighbourhoods.

H. M. D.

Lecture Experiment with Cobaltinitrites. RUDOLF WEGSCHEIDER (*Zeit. anorg. Chem.*, 1906, 49, 441—442).—The experiments described are designed to illustrate some of the properties of cobalt salts.

Sodium cobaltinitrite can be prepared readily by adding to a hot concentrated solution of sodium nitrite a solution of a cobaltous salt, free from nickel, acidifying with acetic acid, and boiling for a few minutes. The solution gives a yellow precipitate of potassium cobaltinitrite with potassium salts, is not precipitated by dilute sodium hydroxide solution in the cold (indicating the absence of Co^{++} and Co^{+++} ions), but yields a precipitate of cobaltic hydroxide on boiling, which shows that the complex salt contains tervalent cobalt and is decomposed by boiling alkalis.

G. S.

Two Remarkable Cases of Isomorphism. H. COPAUX (*Chem. Centr.*, 1906, i, 1673; from *Bull. Soc. franç. Min.*, 29, 77—85).—The acid, $\text{SiO}_2, 12\text{MoO}_3, 2\text{H}_2\text{O}, 31\text{H}_2\text{O}$, and the salt, $\text{SiO}_2, 12\text{MoO}_3, 2\text{Li}_2\text{O}, 29\text{H}_2\text{O}$, crystallise together in varying proportions from cold solutions and from solutions at 30° . The same acid loses $7\text{H}_2\text{O}$ and forms mixed crystals with the salt, $\text{SiO}_2, 12\text{MoO}_3, 2\text{BaO}, 22\text{H}_2\text{O}$, the mixture containing 8—50 per cent. of the acid. These cases show that isomorphism is dependent on similarity of crystalline form and not on chemical composition.

E. W. W.

Zinc-antimony Alloys. S. F. SCHEMTSCHUSCHNY (*Zeit. anorg. Chem.*, 1906, 49, 384—399. Compare Mönkemeyer, *Abstr.*, 1905, ii, 171; Herschkowitz, *Abstr.*, 1898, ii, 582).—From an investigation of the freezing-point curve of zinc-antimony alloys, evidence has been obtained of the existence of the compounds Zn_3Sb_2 and ZnSb . The shape of the curve in the region corresponding with the composition of the latter compound depends on whether the fused mass is brought to crystallisation by the addition of traces of solid alloy, ZnSb , or whether it is allowed to crystallise spontaneously.

The freezing-point curve obtained with inoculation consists of five branches. There is a maximum at 566° and 40 atom. per cent. antimony corresponding with the composition of the compound Zn_3Sb_2 , a break at 537° and 53.7 atom. per cent. antimony, indicating the transition of Zn_3Sb_2 and antimony to the compound ZnSb , as well as two eutectic points at 412.5° and 1.21 atom. per cent. and 505° and 68.5 atom. per cent. of antimony. When the fused mass crystallises spontaneously, there is a eutectic point at 482° and 61.9 atom. per cent. of antimony, the components of the mixture being the compound Zn_3Sb_2 and antimony. Mönkemeyer (*loc. cit.*) found a maximum on the curve corresponding with the composition of the compound ZnSb ,

whereas the author's results, as just described, indicate that the compound in question decomposes into the alloy Zn_3Sb_2 and antimony below its melting point.

The compound Zn_3Sb_2 does not form mixed crystals with either of its components; it exists in two modifications which have a transition point in the neighbourhood of 350° .

From the fact that the electrical conductivity of zinc shows a break at 360° , Le Chatelier (Abstr., 1891, 4) drew the conclusion that a second modification of this metal exists, but the author finds that the cooling curve of zinc shows no break between 150° and 500° .

The paper is illustrated with ten microphotographs.

G. S.

Reduction of Antimony Selenide. PAUL CHRÉTIEN (*Compt. rend.*, 1906, 142, 1339—1341 and 1412—1413).—The complete reduction of antimony selenide by hydrogen is a gradual process; the three lower *selenides* Sb_3Se_4 , Sb_4Se_5 , and SbSe are formed at different stages of the reaction, and the relative velocities of reduction of the three compounds Sb_2Se_3 , Sb_4Se_5 , and SbSe are represented by the numbers 28, 4.3, and 1 respectively. The cooling curve of mixtures of antimony and selenium determined by means of a thermo-electric couple shows four maxima corresponding with the melting points of the triselenide Sb_2Se_3 , and the three new selenides Sb_3Se_4 , Sb_4Se_5 , and SbSe .

The author has redetermined the melting point of antimony and finds it to be 628° ; the last determination due to Krafft is 625° .

The cooling curve of mixtures of antimony and selenium has also been examined by Pélabon (Abstr., 1904, ii, 560; this vol., ii, 173); he obtained a discontinuous curve with two branches parallel to the temperature axis representing the two constant melting points (566° and 518°) of the mixtures containing 11 to 39 per cent. of selenium. The author finds that these results are due to ineffectual stirring; the two temperatures represent the melting points of two mixtures, the liquid not being homogeneous, but consisting of two phases, for on analysing a mixture which had the two melting points 523° and 560° the lower part contained 12.69 and the middle part 32.12 per cent. of selenium.

M. A. W.

Bismuth. JULES ALOY and P. FRÉBAULT (*Bull. Soc. chim.*, 1906, [iii], 35, 396—400).—*Bismuth potassium chloride*, $\text{BiCl}_3 \cdot 2\text{HCl}$, prepared by passing a current of chlorine and bismuth trichloride over potassium chloride heated to redness, is an amber-yellow, crystalline mass, and, though deliquescent, is more stable than bismuth trichloride. The solution in hydrochloric acid, when evaporated, deposits octahedral crystals of the *hydrated salt*.

Bismuth potassium bromide, $\text{BiBr}_3 \cdot 2\text{KBr}$, obtained by passing a current of carbon dioxide, bromine, and bismuth tribromide over red-hot potassium bromide, is crystalline, darkens in colour when heated, and melts at 600° . Water decomposes it, forming bismuth oxybromide and potassium bromide.

Bismuth tribromide hydrobromide, $\text{BiBr}_3 \cdot 2\text{HBr} \cdot 4\text{H}_2\text{O}$, obtained by cooling a solution of the tribromide in hydrobromic acid to -10° ,

forms yellow needles, is deliquescent, and on exposure to air loses hydrogen bromide.

Bismuthates of potassium, KBiO_3 , and sodium, NaBiO_3 , were prepared in an impure state by slowly adding a solution of bismuth nitrate in nitric acid to a concentrated boiling solution of the alkali hydroxide, through which a current of chlorine was passed. The precipitates formed, when washed with water, gradually decomposed. When chlorine was replaced by hydrogen peroxide, anhydrous crystalline products were obtained, varying in colour, with the concentration of the alkali, from deep yellow to chocolate-brown. It is probable that these products consisted of the acid, H_3BiO_4 , in which one or more atoms of hydrogen were replaced by bismuthyl, BiO , and the remainder by the alkali metal, thus: $\text{BiO}_4(\text{BiO})_3$, $\text{BiO}_4\text{K}(\text{BiO})_2$, or $\text{BiO}_4\text{K}_2(\text{BiO})$, &c. T. A. H.

Peroxides of Bismuth. III. ALEXANDER GUTBIER and R. BÜNZ (*Zeit. anorg. Chem.*, 1906, **49**, 432—436. Compare this vol., ii, 174, 234; Deichler, *Abstr.*, 1899, ii, 428).—In former papers the authors have shown that, contrary to the views of Deichler (*loc. cit.*), Pattison Muir, and others, no peroxide of bismuth of constant composition can be obtained by the action of gaseous or electrolytic chlorine on bismuth trioxide suspended in potassium hydroxide solution. Deichler also claimed to have obtained anhydrous bismuth tetroxide by the action of potassium persulphate in alkaline solution on the trioxide, but it is shown in the present paper that the products so prepared resemble in all respects those obtained by the use of chlorine. As before, the most highly oxidised products were obtained with very concentrated potassium hydroxide solution, but it was found that even after several weeks' treatment the wash-water showed an alkaline reaction, and no product of constant composition could be isolated. G. S.

The Attack of Platinum by Sulphuric Acid. L. QUENNESSEN (*Compt. rend.*, 1906, **142**, 1341—1343. Compare Scheurer-Kestner, *Abstr.*, 1876, i, 345; ii, 674; 1878, 650; 1880, 706; Conroy, *Abstr.*, 1903, ii, 433; Delépine, this vol., ii, 24, 93, 289).—Sulphuric acid, containing 94 per cent. H_2SO_4 and free from nitrous acid, has very little solvent action on platinum when the two are heated in a vacuum at 400° , but in the presence of oxygen the platinum is dissolved and the oxygen absorbed, whilst sulphuric acid containing a slight excess of sulphur trioxide in solution dissolves platinum at 400° in a vacuum to the same extent as the more dilute acid in the presence of oxygen. The experiments were conducted on spirals of platinum foil, and the results expressed in grams of metal dissolved per square decimetre per hour are as follows: sulphuric acid, containing 94 per cent. H_2SO_4 , dissolves 0.001 and 0.124 gram commercial platinum in a vacuum and in oxygen respectively, whilst in the case of *pure* platinum the results are 0.0006 and 0.0227 gram; sulphuric acid, containing 2 per cent. of free SO_3 , dissolves 0.0265 gram platinum in a vacuum. M. A. W.

Double Sulphate of Iridium and Potassium, $\text{Ir}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4$. MARCEL DELÉPINE (*Compt. rend.*, 1906, **142**, 1525—1527).—When

potassium or ammonium iridochloride is boiled for several hours with concentrated sulphuric acid, and after addition of potassium sulphate the temperature is gradually raised to 520—530°, the solution assumes a greenish-blue colour. On treating the solidified product with cold water, a greenish-blue powder remains, which dissolves in boiling water, and on cooling rectangular or hexagonal crystals separate, which have the composition $\text{Ir}(\text{SO}_4\text{K})_3 \cdot \text{H}_2\text{O}$.

The potassium salt loses its water at 110°, is completely precipitated by barium and partially by rubidium, strontium, mercury (ous and ic), silver, thallium, bismuth, thorium, quinine, and strychnine solutions. The precipitated salts have a bluish-green colour, and, as in the case of the potassium salt, the contained sulphuric acid is not precipitated by barium solutions; the barium salt, in fact, dissolves in acids without precipitation of any barium sulphate. Ammonia, and the alkali hydroxides and carbonates decompose these complex salts, and the iridium is precipitated in the form of a violet-coloured oxide. The greenish-blue colour of solutions of the potassium salt is changed by reducing agents to a light yellow, but addition of oxidising agents converts the yellow into blue again. Barium sulphate is not precipitated from either the yellow or blue solutions on addition of a soluble barium salt. The observed changes cannot be satisfactorily explained by the formula $\text{Ir}(\text{SO}_4\text{K})_3$.

H. M. D.

Mineralogical Chemistry.

Conditions of Growth of Crystals of Different Forms in a Fluid Medium. P. PAWLOFF (*Zeit. Kryst. Min.*, 1906, **42**, 120—157).—A theoretical discussion, based on thermodynamical principles, of the influence exerted by external conditions (composition and concentration of the solution, pressure, temperature, &c.) on the habit and twinning of crystals during their growth. L. J. S.

Bituminous Lignite ("Schweelkohle"). CARL HÜBNER (*Arch. Pharm.*, 1906, **244**, 196—215).—An account is first given of the work of earlier investigators.

From the portion of the material soluble in benzene but one substance was isolated in a pure state by fractional distillation, namely, a *hydrocarbon*, which melted at 52—53°, contained C 84.92, H 15.14 per cent., and had molecular weight 301 ($C_{22}H_{46}$?); the other fractions still contained oxygen. By treatment of that portion with ether, however, and crystallisation of the soluble and insoluble fractions, two substances were obtained; the first melted at about 77°, and contained C 80.5, H 13.5 per cent. ($C_{16}H_{32}O$?), the second melted at 82—83° and contained C 78.8, H 13.2 per cent. ($C_{12}H_{24}O$?); both substances had the character of saturated *ketones*; when heated they gave off carbon monoxide, but the liquid distillate still contained oxygen, and therefore was not a pure hydrocarbon.

From the portion of the material which was insoluble in benzene, 10 per cent. aqueous sodium carbonate extracted an amorphous *acid*, containing C 60.0, H 4.5, O 27.3, S 8.3 per cent. ($C_{38}H_{34}O_{13}S_2$?); this had the character of a humic acid; when distilled with lime it appeared to yield a mercaptan. Part of the portion insoluble in benzene dissolved in ether; from it an amorphous *acid* was isolated with the character of a humic acid.

C. F. B.

Composition of Chalmersite. EUGEN HUSSAK (*Centr. Min.*, 1906, 332—333).—The previous analysis of this mineral (*Abstr.*, 1902, ii, 267) was made on only 0.016 gram. A further supply of crystals has now been found at the same locality (the Morro Velho gold mine in Minas Geraes, Brazil), and the following new analysis has been made by W. Florence on 0.0896 gram of material carefully separated from intergrown pyrrhotite and copper-pyrites:

Fe.	Cu.	S.	Total.
43.13	22.27	35.11	100.51

This gives the formula $CuFe_2S_3 = Cu_2S, Fe_4S_5$.

The newly-found crystals are almost all simple and are thin-tabular in habit, with angles very near those of copper-glance. Scheelite, titaniferous hæmatite, and regular intergrowths of adularia and albite are recorded from the locality.

L. J. S.

Formation of Quartz and Silicates. JOHANNES KÖNIGSBERGER and WOLF. J. MÜLLER (*Centr. Min.*, 1906, 339—348, 353—372).—Glass or obsidian was heated with water or with water and carbon dioxide or sodium carbonate to about 350° for several hours. The experiments differ from those made previously in the same direction in that the sealed platinum-iridium tube contained a filtering device, so that it was possible to isolate any material which separated during the cooling of the solution, and thus also to determine the composition of the solution at any particular temperature. The substance collected on the filter (that is, which had separated from solution) was usually quartz, sometimes opal, and some undetermined needles, whilst the action of the liquid on the glass resulted in the formation of quartz, chalcedony, tridymite, soda-orthoclase, and ægirine-augite. The bearing of these results on the formation of minerals in the crevices of the crystalline rocks of the Alps is discussed in detail (compare this vol., ii, 235).

L. J. S.

Crystalline Pyrochroite from Långban. HJALMAR SJÖGREN (*Chem. Centr.*, 1906, i, 1759; from *Geol. Fören. Stockholm Förhandl.*, 27, 37).—Pyrochroite occurs in the fissures of the ordinary Långban ore, which are filled with calcite. It is associated with metallic lead in lumps weighing several kilograms, with copper, a considerable quantity of heavy spar, yellow pyroaurite, black earthy manganite, and a mineral which resembles barysilite. The manganite is a decomposition product of pyrochroite. Pyrochroite crystallises in prisms and needles with a distinct basal cleavage, pale sky-blue by daylight and red-

dish-violet by lamplight, but brown when weathered. The mineral has a sp. gr. 3.2435. Analysis gave :

MnO.	FeO.	CaO.	MgO.	H ₂ O.
77.3	0.4	trace	1.7	20.9

E. W. W.

[Palmerite] **New Hydrated Aluminium Potassium Phosphate.** EUGENIO CASORIA (*Chem. Centr.*, 1906, i, 1759; from *Annali R. Scuola Sup. Agric. Portici*, 1904, 6—9).—A new mineral, *palmerite*, has been found under a layer of bat guano in a large cave in the Alburno Mountain, near Controne, in Salerno. It forms a white powder, is unctuous to the touch, and is insoluble in water or acetic acid, but readily soluble in hydrochloric acid, nitric acid, or a solution of ammonium citrate. Analysis gave :

P ₂ O ₅ .	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	K ₂ O.	Na ₂ O.	NH ₃ .	H ₂ O (at 100°).	Loss on ignition.
37.10	0.36	22.89	1.17	8.04	0.02	0.61	7.87	21.29

corresponding with $\text{Al}_2\text{K}_2\text{H}(\text{PO}_4)_3 \cdot 7\text{H}_2\text{O}$.

FERRUCCIO ZAMBONINI points out that $\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 19\text{H}_2\text{O}$ and $\text{Al}_2\text{KH}_2(\text{PO}_4)_3 \cdot \text{Al}(\text{OH})_3 \cdot 7\text{H}_2\text{O}$ also represent the composition of the mineral, and that a similar substance from Misserghin, in Algeria, has been described by Carnot (*Abstr.*, 1896, ii, 34).

E. W. W.

Variety of Thorianite from Galle, Ceylon. WYNDHAM R. DUNSTAN and BERNARD MOUAT JONES (*Proc. Roy. Soc.*, 1906, 77A, 546—549).—The original thorianite (*Abstr.*, 1904, ii, 744) from Balangoda, Ceylon, contained 78—79 per cent. of thoria with 11—15 per cent. of uranium oxides, and it was suggested that the thoria and uranium dioxide formed an isomorphous mixture. This suggestion is confirmed by the following analyses, I—VI, of the new material from Galle, in which uranium is present in larger amount. Analysis I is of small, cubic crystals, and II—VI of larger crystalline fragments; II—IV are of material from different parts of the same fragment, III being from the exterior. The fractured surfaces of the new material are slightly less lustrous and more pitchy in appearance than those of ordinary thorianite, and the mineral has more the appearance of pitchblende; the physical characters are the same as those of thorianite. Analysis VII is of a crystal of ordinary thorianite from Balangoda.

	ThO ₂ , (Ce, La, Di) ₂ O ₃ .	Y ₂ O ₃ .	UO ₂ .	UO ₃ .	PbO.	Fe ₂ O ₃ .	CaO.	H ₂ O.	Insol. in HNO ₃ .	He, CO ₂ .
I.	58.84	0.85	—	32.74	2.56	1.31	0.19	1.26	0.45	present
II.	62.16	1.84	—	10.32 18.88	2.29	1.11	0.59	1.05	0.77	„
III.	66.82		—	28.24	2.29	1.22	0.54	1.00	0.56	„
IV.	—	—	—	28.68	2.50	2.43	—	—	0.54	„
V.	62.32	2.24	—	27.02	2.99	2.28	0.50	2.16	0.87	„
VI.	63.36	1.16	—	27.99	2.90	1.27	0.85	1.32	0.77	„
VII.	78.98	1.47	—	13.40	2.54	0.87	0.91	1.28	0.47	„

The radioactivity of ordinary thorianite (containing 78·86 per cent. thorium) has been determined by R. J. Strutt to be 1·16 times stronger than that of the new variety (containing 58·84 per cent. thorium, anal. I).
L. J. S.

Gyrolite and other Zeolites from Brazil. EUGEN HUSSAK (*Centr. Min.*, 1906, 330—332).—Veins in a quarry newly opened in diabase at Mogy-guassù, in São Paulo, Brazil, contain crystals of calcite with gyrolite, laumontite, and apophyllite. The gyrolite forms spherical aggregates, 2 cm. in diameter, of thin, radially arranged plates; it is white or pale to dark green in colour. Cleavage flakes are seen to be optically uniaxial and negative. Analysis I, by G. Florence: the dark green variety contains: $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$, 7·36; MnO, 0·32 per cent. Enclosed in the gyrolite are needles of laumontite, and encrusting its surface are minute and brilliant cube-like crystals of apophyllite.

	SiO_2 .	Al_2O_3 .	CaO.	Na_2O .	K_2O .	H_2O .	Total.	Sp. gr.
I.	52·77	0·73*	33·04	0·35	0·41	12·58	99·88	2·409
II.	51·94	20·09	11·40	0·77	0·48	16·10	100·78	2·321

* Including trace of Fe_2O_3 .

Laumontite (anal. II) occurs as white, acicular crystals, which are usually twinned on $a(100)$, and sometimes as intercrossing twins with a dome-face as twin-plane.
L. J. S.

Axial Ratios of Sillimanite. E. TAUBERT (*Centr. Min.*, 1906, 372—373).—The length of the vertical axis of sillimanite has not hitherto been determined. On a small crystal from Chester, in Connecticut, a terminal face was observed to which the indices (052) are assigned. The axial ratios are $a : b : c = 0·9696 : 1 : 0·7046$. On theoretical grounds, G. Linck, in 1896, had calculated $c = 0·70048$.
L. J. S.

Some Minerals from the Tourmaline Lodes of the Granite of S. Piero in Campo (Elba). GIOVANNI D'ACHIARDI (*Chem. Centr.*, 1906, i, 1759; from *Proc. Verb. Soc. Toscana Sci. Nat. Pisa*, 14, 89—96).—Pyrites and mispickel have been found for the first time in the tourmaline lodes of the granite of S. Piero.

Stilbite derived principally from Fonte del Prete yielded on analysis :

SiO_2 .	Al_2O_3 .	CaO.	K_2O , Na_2O .	H_2O (at 110°).	Loss on ignition.
57·91	15·85	7·88	0·68	2·73	15·64.

Also traces of Fe_2O_3 and MgO.

E. W. W.

Products of the Recent Eruption of Vesuvius. ALFRED LACROIX (*Compt. rend.*, 1906, 143, 13—18).—Chemical analyses and petrographical descriptions are given of the different types of material. Analysis I is of the scoria ejected at the commencement of the eruption during the Strombolian stage, and II of the lava stream which flowed subsequently; the two analyses show that the magma did not vary in composition. Analysis III is of the scoria and lapilli which

overwhelmed Ottajano, and IV of the fine ash. These differ in composition from the magma owing to intermixture with earlier materials building the volcanic cone:

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	CaO.	Na ₂ O.	K ₂ O.	TiO ₂ .	P ₂ O ₅ .	Ign.	Total.
I.	47.50	18.59	1.52	7.62	3.86	9.16	2.72	7.05	1.05	trace	1.25	100.02
II.	48.28	18.39	1.12	7.88	3.72	9.20	2.84	7.25	1.28	0.51	0.62	100.96
III.	48.10	15.31	3.20	5.45	7.55	12.45	1.98	4.22	1.15	0.12	0.87	100.28
IV.	48.00	16.10	3.35	4.90	6.53	11.35	3.04	5.26	1.02	trace	0.25	100.29

* Also Cl, 0.49.

L. J. S.

Vesuvian Ash from the Baltic; Gypsum in Vesuvian Ash. REINHARD BRAUNS (*Centr. Min.*, 1906, 321—327).—A fine yellow dust, which fell at Neustadt, in Holstein, on April 14, while a south wind was blowing, was found to consist of mineral particles measuring 0.05—0.005 mm. in diameter, the largest being 0.1 mm. The minerals identified, leucite, felspar, olivine, augite, and also a pale brown glass, are those characteristic of Vesuvian lava (leucite-basanite); quartz is absent, and the only foreign substances are particles of soot and pollen grains. Ash collected at various places in the immediate neighbourhood of Vesuvius during the eruption had the same characters. The latter, when extracted with water, was found to contain gypsum to the extent of $2\frac{1}{2}$ to 3 per cent.; this has no doubt originated by the oxidation of sulphur dioxide. A saline encrustation on the new Vesuvian lava was found to consist mainly of ammonium chloride, with which is probably some sodium silicofluoride.

L. J. S.

Presence of Gold and Silver in the Trias of Meurthe-et-Moselle. FRANCIS LAUR (*Compt. rend.*, 1906, 142, 1409—1412).—Analyses of borings made at Raucourt and adjoining places in Meurthe-et-Moselle show that they nearly all contain traces of gold and silver, and a limestone grit taken at a depth of 382 m. (? 582 m.), containing 39 grams of gold and 245 grams of silver per ton, had the following percentage composition:

SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	CaSO ₄ .	CaO.	MgO.	Au, Ag.	Loss on ignition.
23.88	0.18	19.59	7.85	21.82	0.2	0.2284	26.64

Also traces of phosphoric acid.

M. A. W.

Changes in the Composition of Sea Water on Freezing. WILHELM E. RINGER (*Chem. Centr.*, 1906, i, 1674; from *Chem. Weekblad*, 3, 223—249).—Although the eutectic point of sodium sulphate is -0.7° it does not separate from sea water at temperatures above -8° . The ice in which this salt is partially deposited originally contains some of the mother liquor with which the ice was in equilibrium at the temperature of deposition. As diffusion, &c., causes the mother liquor to be replaced by "fresh sea water, ice and salt again separate until the residual liquid attains the original concentration," the process may go on until all or nearly all the mother liquor has been removed. When the ice laden with sodium sulphate passes to warmer regions it does not give up the sulphate at the temperature at which it was

deposited, but, if all the mother liquor has been eliminated, melts at -0.7° , and thus affects the quantity of sulphate contained in the water to a considerable distance. The behaviour of sodium chloride is similar, but the changes are less marked, as there is less difference between the eutectic point and the temperature of separation. The determination of the ratio of the quantity of calcium oxide to that of chlorine may suffice, however, in some cases to indicate the origin of the water. A distinct change in the ratio would show that the water had been cooled below -23° .

The separation of potassium and magnesium chlorides can occur only seldom.

E. W. W.

Analysis of the Water of Death Gulch. GEORGE B. FRANKFORDER (*J. Amer. Chem. Soc.*, 1906, 28, 714—717).—It is stated that in Death Gulch, a narrow ravine in Yellowstone National Park, Minn., obnoxious gases accumulate which are fatal to animals, and it has been considered possible that this may be partly due to the water of a little stream which flows through the ravine. A sample of the water which was examined had a peculiar yellowish-green colour, was strongly acid, and at the time of analysis contained all the iron in the ferric state. The following results were obtained, which are expressed in grams per litre: SiO_2 , 0.8100; Al, 1.9438; Fe, 8.3173; Ca, 0.3142; Mg, 0.0080; Na, 0.9069; K, 0.1489; SO_4 , 42.2904; Cl, 1.0326. After the water had been kept for several months it was darker in colour, somewhat resembled commercial sulphuric acid, and had a sp. gr. 1.05156; at the bottom of the bottle a deposit of sulphur and silica had collected.

E. G.

Physiological Chemistry.

Effects of Injection of Antitoxic and Antibacterial Sera on the Opsonic Power of the Blood. WARRINGTON YORKE and C. HAROLD SMITH (*Bio chem. J.*, 1906, 1, 341—346).—Injection of antitetanic serum was found to raise the tetano-opsonic index; this was followed by a fall, and the index was also found to be low with tubercle and staphylococcus. Coincidentally with this a rash appeared, and then the opsonic power of the blood returned slowly to normal. Similar results were obtained with other antitoxic sera. The sera used did not contain opsonins, although they must have contained them when freshly prepared. The preliminary rise in the index may be due either to a substance in the serum which is easily converted into opsonin, or more probably the body is stimulated to produce opsonins under the influence of the vaccine injected. The subsequent depression is much more marked, and this is attributed to the influence of toxic materials in the serum; the toxic effects in addition are skin rashes, œdema,

albuminuria, a feeling of debility, and an injury to the red corpuscles which enables the leucocytes to attack and absorb them.

W. D. H.

Chemical Conditions for Heart Activity, with Special Reference to the Heart of Limulus. A. J. CARLSON (*Amer. J. Physiol.*, 1906, 16, 378—408).—Isotonic solutions of the non-electrolytes sugar, urea, and glycerol act on the muscle and nerve endings in the heart of the king-crab as depressants, whilst on the heart ganglion they are primarily stimulants. The specific influence of the salts of the blood (sodium, magnesium, ammonium, and potassium salts) on the heart's action is the same as in vertebrates; they act primarily on the ganglion, but the influence of calcium salts is exactly the opposite to that which occurs in the vertebrate heart.

Matthews' view, that all anions stimulate and all cations depress protoplasmic activity, has been extended to the heart by Benedict; in the present research the exceptions to this rule appear to be as numerous as the cases where it holds.

W. D. H.

The Action of Ethyl Alcohol and related Alcohols on the Frog's Heart. HERMANN DOLD (*Pflüger's Archiv*, 1906, 112, 600—622).—The application of various alcohols, either by perfusion or otherwise, to the frog's heart, first stimulates, then paralyses, and finally kills it. The primary stimulating effect can only be demonstrated with very dilute solution, especially in the case of the higher alcohols. The harmful action is most readily seen with the higher alcohols. The question is discussed whether, if these observations are applicable to the warm-blooded heart, the effect of alcohol during life is due to its effect on the heart itself or on the central nervous system. Probably both factors are concerned, but the effect on the nervous system is regarded as paramount. The local effect on the heart of strong solutions, or in chronic alcoholic poisoning, is evident from the anatomical changes it undergoes.

W. D. H.

The Iodine Reaction in Leucocytes. J. BARNICOT (*J. Path. Bact.*, 1906, 11, 304—332).—The intracellular iodine reaction, although faintly seen in normal, is much more marked in pathological, blood, and indicates degeneration (not increased activity for purposes of defence) due to toxæmia. It bears no relation to leucocytosis. Its continued presence in pneumonia should lead to complications being suspected. When an accumulation of pus is thought to exist, a negative reaction would lead to the accuracy of the diagnosis being doubted. Apart from these two practical points, the reaction is too inconstant to be of much help either in diagnosis or prognosis.

W. D. H.

Hæmolysin Formation. IVAR BANG and J. FORSSMAN (*Beitr. Chem. Physiol. Path.*, 1906, 8, 238—275).—Ehrlich's side-chain theory is criticised. After the amboceptor has acted on the blood corpuscles, and prepared a way for the action of the complement (perhaps by

acting on the lipsoïd membrane), the latter acts directly on the corpuscle without needing any linking by means of the amboceptor.

W. D. H.

Nature of Precipitin-reaction. HARTOG J. HAMBURGER and SVANTE ARRHENIUS (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 33—45).—On adding to a fixed quantity of calf-serum (precipitin) increasing quantities of diluted horse serum (precipitinogen substance), the amount of precipitate formed at first increases, but finally decreases again. An equilibrium reaction following the law of Guldberg and Waage takes place, whereby only a certain quantity of the two components combine together, the rest remaining in the free state. The additive compound is partly precipitated and partly dissolved, the amount in solution depending mainly on the proportion of salt solution present, since the sediment is soluble in sodium chloride.

Alongside this equilibrium there is another caused by the precipitate in part combining with free precipitinogen substance and forming a soluble compound.

E. F. A.

Precipitins produced by Chemically-allied Proteids. FRITZ OBERMEYER and ERNST P. PICK (*Chem. Centr.*, 1906, i, 1791; from *Wien. klin. Woch.*, 19, No. 12).—If immunity is produced by boiled serum proteid of the ox, the serum contains a precipitin which is specific to various derivatives of proteids used. A specific immune serum is also obtainable with products of tryptic digestion. This specificity is believed to be related to the constitution of the proteid molecule, and is termed constitutional specificity.

W. D. H.

The Fat-splitting Ferment in the "Little Stomach." ERNST LAQUEUR (*Beitr. chem. Physiol. Path.*, 1906, 8, 281—284).—By using Pawloff's method of the "little stomach" in dogs, the ferment described by Volhard as being able to split fat if in the form of a fine emulsion was found secreted with the gastric juice. Its action is hardly, if at all, increased by the presence of bile.

W. D. H.

Influence of Autolysis on the Pentose of the Pancreas. PHILIP HENRY MITCHELL (*J. Biol. Chem.*, 1906, 1, 503—506).—No pentose is lost during prolonged autolysis in the absence of bacteria, neither is it diminished by peptic digestion. The destructive effects of putrefaction on pentose described by Ebstein are confirmed.

W. D. H.

Rôle of Cellular Elements in the Digestion of Carbohydrates by Intestinal Juice. H. BIERRY and ALBERT FROUIN (*Compt. rend.*, 1906, 142, 1565—1568).—The clear liquid obtained after thorough washing from an intestinal loop is regarded as its physiological secretion; it contains only maltase. The other enzymes which the intestinal juice is stated to contain (amylase, sucrase, trehalase) originate from the disintegration of, or diffusion from, epithelial cells.

W. D. H.

Intermediary Metabolism in the Anaërobie Stage of the Pupæ of Calliphora. ERNST WEINLAND (*Zeit. Biol.*, 1906, 48, 87—140. Compare Abstr., 1905, ii, 734).—Gas formation occurs in a mass of the pupæ, which is not of bacterial origin. It consists of carbon dioxide and hydrogen in the proportion by volume of 2 to 1, and thus corresponds with the gases resulting from the decomposition of carboxyl. It is not formed from carbohydrate, but mainly, or perhaps wholly, from fatty acids. An analogous decomposition occurs when finely divided rhodium or iridium acts on formic acid. If the animals are shaken with air or oxygen the carbon dioxide is still formed, but hydrogen occurs either in small quantities or not at all. Probably this represents the normal course of things in the intact animal. If the animal is in the condition to liberate nascent hydrogen it possesses a powerful means of reduction.

W. D. H.

Influence of Sodium Nitrite on Metabolism. N. F. SURVEYOR (*Bio-chem. J.*, 1906, 1, 347—354).—Sodium nitrite injected subcutaneously in dogs raises the amount of water eliminated by the kidneys and rectum, causes an increase in the excretion of urea and nitrogen, an increased absorption of nitrogen and fat by the alimentary canal, and an increase of body weight. The beneficial influence, if any exists, of the drug in syphilis and in nervous affections following that disease is probably due to the improved nutrition of the organism.

W. D. H.

Action of Asparagine on Nitrogenous Metabolism. CURT LEHMANN and FRANZ ROSENFELD (*Pflüger's Archiv*, 1906, 112, 339—351).—The conditions under which amino-substances are mixed with the food form an important factor in influencing nitrogenous metabolism. By delaying their solution, the nitrogenous constituents of the body are better obtained and eventually increased. Hitherto experiments with asparagine have been carried out by adding it directly in solution to the food; hence the unfavourable results noted. Under natural conditions, it is enclosed within the cells or divided over a large volume of food, so that absorption is slow, and it is more completely broken up by bacterial action.

W. D. H.

Behaviour of certain Amides Alone and in Combination in Carnivorous Metabolism. W. VÖLTZ (*Pflüger's Archiv*, 1906, 112, 413—438).—Various amino-compounds (asparagine, acetamide, glycine, &c.) differ in their behaviour both as regards nitrogen metabolism and calorific value. The firmly combined amino-group in glycine produces less elevation of the nitrogenous exchanges than does acetamide, in which the group is loosely held. Better results on equilibrium are obtained by using a mixture than by giving these substances singly. Incorrect conclusions are thus apt to be drawn if single substances are experimented with, for in ordinary nutrition a mixture is given.

W. D. H.

Influence of Phosphoric Acid and Phosphates of Sodium on Metabolism. ALEXANDRE DESGREZ and Mlle. BL. GUENDE (*Compt. rend.*, 1906, 142, 1440—1442).—The elaboration of nitrogenous matter in

guinea-pigs is increased by phosphoric acid, dihydrogen sodium phosphate, and sodium phosphate; the effect increases with the acidity of the molecule. Catabolism is increased in greater proportion than anabolism. The "dimineralisation" of the organism is not increased by phosphoric acid as it is by hydrochloric acid and organic acids.

W. D. H.

The Ferments which participate in Nuclein Metabolism. WALTER JONES and C. R. AUSTRIAN (*Zeit. physiol. Chem.*, 1906, **48**, 110—129).—Differences are noted in different organs and in different animals; thus, pig's liver contains adenase and xantho-oxydase, but not guanase, and differs from the spleen in the presence of the oxydase. Pig's pancreas contains guanase and adenase, but not oxydase. The dog's spleen contains all these ferments, and the liver contains guanase, only a trace of adenase, and no oxydase. The rabbit's liver contains guanase and oxydase, but not adenase.

W. D. H.

Muscular Work and Proteid Metabolism. W. W. SAWJALOFF (*Zeit. physiol. Chem.*, 1906, **48**, 85—86).—The perfusion fluid flowing out from the isolated heart of cats and rabbits does not contain urea or ammonia after one and a half to two and a half hours' work. The work is therefore independent of proteid metabolism.

W. D. H.

Feeding Experiments with Simple Food-stuffs on Pigeons and Rats. LUDWIG JACOB (*Zeit. Biol.*, 1906, **48**, 19—62).—Previous researches on the influence of pure food-stuffs on animals, although they are contradictory on many points, lean in the main to the conclusion that the absence of the ordinary mixed diet is harmful. In the present research, pure starch, olive oil, casein sugar, salts, and cellulose will serve as examples of the materials employed. The absence of tasty admixtures has been regarded as a cause of failure of appetite. In pigeons, however, the diet was followed by no ill results; the same is true for the rats experimented on.

W. D. H.

The Fate of Carbon Monoxide in the Animal Body. FRANZ WACHHOLTZ, FRANZ WORGITZKI, and OTTO WEISS (*Pflüger's Archiv*, 1906, **112**, 361—397).—The mealworm possesses in a high degree the power of causing carbon monoxide to disappear from an atmosphere containing that gas. Mice, rabbits, pigeons, and earthworms do not possess this capacity.

W. D. H.

Rôle of Sodium Chloride in the Histological Impregnation of Tissues by Silver Nitrate. CH. ACHARD and M. AYNAUD (*Compt. rend.*, 1906, **142**, 1571—1572).—The well-known histological reduction staining with silver nitrate is attributed to the presence of sodium chloride in the tissues. [The authors do not mention the similar conclusion already reached by Macallum (*Abstr.*, 1905, ii, 736; this vol., ii, 182).]

W. D. H.

The Effects of Magnesium and Calcium on the Rhythmical Contractions of a Jelly-fish (Polyorchis). JACQUES LOEB (*J. Biol. Chem.*, 1906, **1**, 427—436).—The rhythmical swimming motions of this

animal only occur in such solutions as contain magnesium, and their apparent spontaneity depends on the magnesium in sea water. The magnesium effect can be inhibited by equivalent amounts of calcium or potassium. The isolated centre of *Polyorchis*, which will not beat in sugar solution or sea water, does so in both when a certain amount of the chloride of either calcium, strontium, or barium is added. If at least four times the equivalent amount of magnesium is then added, the stimulating effect of the calcium is inhibited. It will not beat, as a rule, in sodium chloride solution; it may be made to beat by any of the decalcifying salts (oxalates, fluorides, oleates, citrates, &c.) or by acids. Alkalis inhibit the beats. W. D. H.

Post-mortem Disappearance of Glycogen in the Muscles. FRANZ KISCH (*Beitr. chem. Physiol. Path.*, 1906, 8, 210—237).—The disappearance of glycogen from the muscles after death is not to be regarded as a "vital" action of the surviving tissue, but as due to the activity of a diastatic ferment. The rate of disappearance differs in different muscles and different animals, and is related to alterations of alkalinity. The possible rôle of such a ferment during life, and its relation to the oxygen supply brought by the blood and to certain pathological conditions, are discussed. W. D. H.

Meat Extracts. FRIEDRICH KUTSCHER (*Zeit. Nahr. Genussm.*, 1906, 11, 582—584).—The author has separated two bases, neurine and choline, from Liebig's meat extract, the occurrence of which in this extract has not been recognised previously. They do not appear to be present in all samples of the extract. W. P. S.

Formation of Adrenaline in the Organism. WALTER L. HALLE (*Beitr. chem. Physiol. Path.*, 1906, 8, 276—280).—The theory of the formation in the body of adrenaline from tyrosine is advanced, with experiments showing that certain enzymes produce an action on tyrosine, and that the addition of tyrosine to finely-minced suprarenal gland leads to an increased yield of adrenaline. The author admits that the theory still requires more stringent proofs. W. D. H.

Catalase. ERNST J. LESSER (*Zeit. Biol.*, 1906, 48, 1—18).—A comparison of the catalase action of tissues of different organisms shows that it is least in the anaërobic animal, *Ascaris*. Another parasite, however (*Distoma hepaticum*), has a powerful action: this is possibly due to the fact that it lives partly on the blood of its host, and so is accustomed to oxygen. No marked difference was found between the tissues of cold- and warm-blooded animals in this direction. The tissues, however, vary greatly amongst themselves, and the reason for this is not apparent. Differences are also noted in vegetable tissues. The decomposition of hydrogen peroxide by catalase does not lead to the oxidation of fat or carbohydrate. W. D. H.

The Soluble Proteids of Milk. LÉON LINDET and LOUIS AMMANN (*Compt. rend.*, 1906, 142, 1282—1285).—Hammarsten's theory that in milk curdling by rennet the caseinogen is decomposed into casein and a

soluble proteid is regarded as untenable, and one applying the physical nature of the coagulation of colloids should be substituted. Rennin causes only a part of the previously soluble caseinogen to appear in the curd, the remainder as phospho-caseinate in colloidal suspension remains in the whey. The whey also contains lact-albumin; the existence of lacto-globulin is regarded as problematical. In order to estimate the lact-albumin, filtration through kaolin is recommended to remove the caseinogen.

W. D. H.

Action of Single Foods on Milk Production. AUGUST MORGEN, CARL BEGER, and GUSTAV FINGERLING (*Landw. Versuchs-Stat.*, 1906, 64, 93—242. Compare Abstr., 1904, ii, 750; 1905, ii, 649).—Addition of fat to an insufficient amount of food deficient in fat and proteid considerably increased the yield of milk and milk constituents, as well as the amount of fat in the milk and in the dry matter. Addition of proteid resulted in a still greater increase of milk and of milk constituents with the exception of fat. The nature of the milk fat was affected by fat alone, which raised the refractometer number.

When proteid was substituted by a thermal equivalent of fat, the yields of milk, dry matter, sugar, and nitrogenous matter were diminished, whilst the effect on milk fat production was favourable. Proteids increase the yield of milk more than fat does, but have less effect on fat production.

Addition of lecithin to food seemed to increase the yield of milk, but was only favourable to the production of milk fat when fed in conjunction with foods deficient in fat. Lecithin also gave rise to an increase in live weight.

The results of the whole series of experiments (six years) indicate that fat alone has a specific action on the production of milk fat, proteids and carbohydrates having no such action. Within certain limits, fat is therefore the most suitable substance for milk fat production.

N. H. J. M.

Effect of Different Fats, both Emulsified and not Emulsified, on the Production of Milk. CARL BEGER (*Landw. Versuchs-Stat.*, 1906, 64, 249—252. Compare preceding abstract).—Earth-nut oil increased the yield of milk, dry matter, and fat more than palm oil and hay fat, but lowered the percentages of dry matter and fat in the milk. The action of hay-fat was similar to that of palm oil, but somewhat less. In the case of goats, butter-fat gave the best results, then earth-nut oil, and lastly palm oil.

Feeding with palm oil resulted in a lowering of the refractometer number of the milk fat.

The results of previous experiments with emulsified fats failed to show any advantage in the case of emulsions, possibly owing to insufficient emulsification.

N. H. J. M.

Secretion by the Renal Tubules in the Frog. FRANCIS A. BAINBRIDGE and ARTHUR P. BEDDARD (*Bio-chem. J.*, 1906, 1, 255—273).—The experiments, a preliminary account of which has already appeared (this vol., ii, 469) prove that the renal tubules

secrete urea, chlorides, sulphates, dextrose (during hyperglycæmia and after phloridzin injection), and probably creatinine and phosphates, in fact most of the normal urinary constituents. The glomerular epithelium is also to be regarded as secretory, and the theories which regard the glomerular function, as filtration, and the tubular epithelium as absorption, are criticised. The only known difference between the urines secreted by the glomerulus and the tubules is that the former is always, and the latter never, acid to acid magenta. The power of the glomeruli to get rid of fluid is in general assisted by increased blood flow, but can take place independently of this. It seems impossible to explain diuresis following injury to the bulb without assuming the presence of secretory nerves, and nerve-endings have been described by Berkeley in the renal epithelium. W. D. H.

Diuresis. XII. Excretion of Sodium Chloride during Phloridzin Diuresis. JOH. BIBERFELD (*Pflüger's Archiv*, 1906, 112, 398—412).—In phloridzin diuresis, both the percentage and absolute amount of sodium chloride excreted sinks; the drug interferes with the power of the kidney to excrete this substance. The bearing of this observation on the filtration theory of urine formation, and especially on Löwi's views, is discussed. W. D. H.

Urea in Human Urine. FRITZ LIPPICH (*Zeit. physiol. Chem.*, 1906, 48, 160—179).—The chief quantity of the urea as estimated by approved methods is doubtless carbamide. At any rate, no substance corresponding with Moor's urein was found. W. D. H.

Influence of Chocolate and Coffee on Uric Acid [Excretion]. PIERRE FAUVEL (*Compt. rend.*, 1906, 142, 1428—1430).—The methyl-xanthines of chocolate and coffee increase the amount of purine bases in the urine, but have no effect on uric acid excretion; the precipitation of uric acid by acids is prevented. The influence of these substances, especially of theobromine, is thus less pernicious than that exerted by the purine substances of meat and leguminous plants. W. D. H.

Excretion of Endogenous Purine Substances and Uric Acid. PIERRE FAUVEL (*Compt. rend.*, 1906, 142, 1292—1294).—On a diet free from purine, the amount of purine substances and uric acid excreted remains constant in the same person, but varies in different people. [This has already been found to be the case by other observers (for instance, Burian) but no reference to the work of these is given.] W. D. H.

Purine Substances of the Urine of Ox, Horse, and Pig. ALFRED SCHITTENHELM and ERNST BENDIX (*Zeit. physiol. Chem.*, 1906, 48, 140—144).—Differences in the proportion of uric acid and purine bases in different animals are illustrated by analyses, and appear to depend on the differences in the enzymes present which take part in nuclein metabolism. Special attention is directed to the high percentage of guanine in pig's urine from animals suffering from "guanine-gout." The base also accumulates in the tissues. W. D. H.

Excretion of Antipyrine by the Human Organism. D. JONESCU (*Chem. Centr.*, 1906, i, 1794; from *Ber. deut. pharm. Ges.*, 16, 133—140).—Experiments have shown that antipyrine does not combine with glycuronic acid in the human organism. Free antipyrine is found in the urine, and it is only after considerable doses that it occurs partially combined with sulphuric acid. E. W. W.

The Amount of Sulphur-containing Substances in Human Fæces. FELIX VON OEFELE (*Chem. Centr.*, 1906, i, 1754—1755; from *Ber. deut. pharm. Ges.*, 16, 82—93).—Comparative tables are given of the amount of sulphur-containing substances in fæces, and the methods for estimating them. About one-third of the total sulphur originates from the taurine of the bile. W. D. H.

Lactic Acid Formation in Cancer of the Stomach. KONRAD SICK (*Chem. Centr.*, 1906, i, 1797; from *Arch. klin. Med.*, 86, 371—399).—Long bacilli producing lactic acid grow readily in the stomach of cancer patients, for the hydrochloric acid of the gastric juice is scanty or absent. If very little proteid is present, the production of lactic acid is less, although volatile fatty acids are still formed. The formation of the acid goes up on the administration of proteid in the form of extract of carcinoma, or of numerous organs, or blood serum. W. D. H.

Acidity of the Gastric Contents [in Cancer]. BENJAMIN MOORE, W. ALEXANDER, R. E. KELLY, and HERBERT E. ROAF (*Biochem. J.*, 1906, 1, 274—296). **Hæmalkalimetry.** BENJAMIN MOORE and FRED P. WILSON (*ibid.*, 297—327. Compare *Abstr.*, 1905, ii, 741).—Any enfeeblement in general condition leads to diminution of the gastric acid, but this is most marked in cancer in whatever region of the body the new growth takes place. This conclusion is reached after the examination of a larger number of cases than in previous publications. Free hydrochloric acid was entirely absent in two-thirds of these. This points to a change in the concentration of hydrogen ions in plasma and lymph. The alkalinity of the inorganic constituents of the plasma is increased in cancer. Increased alkalinity stimulates cell growth, and may lead to the excessive nuclear division of malignant disease.

The second paper deals mainly with methods, and a discussion of the results with special reference to cancer. The results of physical methods show that the ratio of the concentration of hydrogen and hydroxyl ions in the blood plasma is a comparatively low one, thus indicating an approximation to neutrality; yet the cells are extremely sensitive to small variations in this ratio. The only approximate method available is that of determining the *reactivity* of the plasma or serum to acids or alkalis by means of indicators. The resistance of the serum to rapid displacement of the ratio in the two ions when acid or alkali is added, is termed its reactivity. The amount of alkaline reactivity may be determined by titration with acid in the presence of a strong indicator, such as dimethylamino-azobenzene or methyl-orange, which changes with a concentration of hydrogen ions somewhat higher

than that of distilled water. The amount of acidic reactivity may be determined by titration with alkali in the presence of a weak indicator, such as phenolphthalein, which changes with a concentration in hydroxyl ions somewhat higher than in distilled water. The increased alkalinity in cancer is regarded rather as a cause than an effect of the disease. It is less after removal of the proteids, which indicates that the proteids in cancer possess a higher basic reactivity than normal.

W. D. H.

Intra-ocular Lipæmia and Diabetes. W. HALE WHITE (*J. Path. Bact.*, 1906, 11, 371—372).—The lipæmic condition of the blood, which can be recognised during life by examining the intra-ocular blood vessels, is not "exceedingly rare." In some cases, however, the milky appearance is not due to fatty, but to proteid granules (compare Turney and Dudgeon, this vol., ii, 109).

W. D. H.

The Utilisation of Carbohydrate in Cases of Diabetic Arthritis. RENÉ LAUFER (*Compt. rend.*, 1906, 143, 74—77).—Two cases are described, in which intolerance to a diet mainly composed of proteids and fats was exhibited, with an increase of glycosuria and nitrogenous breakdown. A mixed diet containing carbohydrate is recommended; this increases the utilisation of nitrogen, and does not, within certain limits, increase the glycosuria.

W. D. H.

Leucæmia and Chloroma. G. LOVELL GULLAND and ALEXANDER GOODALL (*J. Path. Bact.*, 1906, 11, 333—363).—Acute and chronic lymphatic leucæmia and chloroma are all essentially the same. The bone-marrow is the starting point and essential seat of the disease. The overgrowth which occurs there and in the marrow cells carried by the blood to other organs is of the nature of tumour growth. The excess of cells leads to phagocytosis of cells in other parts and of red blood corpuscles; the latter fact accounts for the anæmia seen.

W. D. H.

Physiological Action of Ethyl Chloride, Bromide and Iodide and of Somnoform. W. WEBSTER (*Bio-chem. J.*, 1906, 1, 323—340).—These four anesthetics act in the same way; the differences between them are of degree only and depend on their volatility. Small doses increase the frequency and depth of respiration; larger doses lessen both; very large doses stop respiration before the heart. Small doses raise slightly, and larger ones depress, the arterial pressure; this depends on action on the heart. The drugs are stated not to paralyse vagus nerve-endings, as Cole found.

W. D. H.

Action of Adrenaline on Muscular Glycogen. Z. GATIN-GRUZEWSKA (*Compt. rend.*, 1906, 142, 1165—1167).—In the diabetic condition in rabbits produced by the injection of 1 to 2 mg. of adrenaline, the muscular glycogen rapidly disappears, and twenty-four hours after the injection none is left.

W. D. H.

The Effect of Sulphurous Acid and Sulphites on Health, with Special Reference to the presence of Free Sulphurous Acid. HERMANN WALBAUM (*Arch. Hygiene*, 1906, 57, 87—144).—This is a contribution to the question of sulphites in food as a preservative. The harmfulness of the admixture is mainly proved by experiments on animals. The main symptoms are due to free sulphurous acid liberated in the organism, especially by the gastric acid. They indicate paralysis of the central nervous system. W. D. H.

Ion-Proteid Compounds. III. Influence of Electrolytes on the Toxicity of Alkaloids. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1906, 1, 507—557. Compare this vol., ii, 376).—Various salts investigated exercise a definite action on the toxicity of a number of alkaloids in relation to paramœcium and other simple animals. The results lend support to the idea of the existence in protoplasm of an unstable ion compound which is readily replaceable by other ions in accordance with the laws of mass action. Possible applications of such a hypothesis to physiological investigations and therapeutics are discussed. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Destruction of Bacteria by Light. HERMANN THIELE and KURT WOLF (*Arch. Hygiene*, 1906, 57, 29—55).—The experiments were made with every possible care, the bacteria being kept in a liquid nutrient medium, stirred by a stream of gas bubbles in a quartz tube, which was immersed in a large vessel of conductivity water provided with a quartz window through which the light entered. An arc lamp, or a quartz mercury lamp, was used as the source of light. Under the working conditions, the bacteria were destroyed by the light ray in about 15 minutes with the arc, and in $7\frac{1}{2}$ minutes with the mercury lamp, the latter being brought to within 4.5 cm. of the quartz window. There is no evidence in favour of the view that the destruction by the light is due to its acting indirectly in oxidising water to hydrogen peroxide even in presence of oxygen. At first a physiological salt solution in Elbe water was employed as nutrient; subsequently, bouillon in a dilution of 1 : 1000 was used, this latter being perfectly transparent for ultra-violet rays.

Light which had been filtered through solutions of nitrates or of oxalic acid was without action on the bacteria; disodium phosphate and potassium thiocyanate solutions allowed active light capable of killing the bacteria to pass through. This active bactericidal region lies therefore between the beginning of the oxalic acid absorption spectrum and that of potassium thiocyanate, namely, from 265—300 μ , and is in the same region as the maximum of intensity of the arc lamp—288 μ . The bacteria were exposed to the action of ultra-violet light alone by

filtering the light through pieces of blue rock salt crystal, and under these conditions were destroyed within a short time. E. F. A.

Energy-Metabolism in Certain Bacteria. Spontaneous Heat-formation in Cow's Milk and the Lactic Acid Fermentation. MAX RUBNER (*Arch. Hygiene*, 1906, 57, 193—243, 244—265).—The first paper is a study in "energetics" from the general point of view. The second deals with a particular instance. The lactic acid fermentation should by calculation, *cæteris paribus*, develop from a third to a half as much heat as the alcoholic fermentation, but in milk this is still further diminished by the fact that the lactic acid fermentation ceases when the percentage of the acid has risen to 1.6. The actual heat developed in milk is about twice as great as that which can be accounted for by the energy of the lactic acid fermentation; a small additional amount is accounted for by the neutralisation of phosphates. The remainder must be the result of other processes, or other micro-organisms, acting possibly on fats and proteids. No heat development could be detected, however, in the change of caseinogen into casein.

W. D. H.

Bacterial Growth and Concentration of Nutrition (Nitrogen and Sulphur Metabolism). MAX RUBNER (*Arch. Hygiene*, 1906, 57, 161—193).—Growth is only one manifestation of energy, especially in early life, and the increase of bacterial cultures rises with the concentration of the nutriment in the media, although not in strict proportion. As measured by the amount of nitrogenous and especially sulphur exchanges, metabolism is more active in dilute solutions.

W. D. H.

Chemistry of the Bacillus Coli Communis, MARY F. LEACH (*J. Biol. Chem.*, 1906, 1, 463—502).—The cell substance of this bacillus yielded about 8.5 per cent. of ash and 3 per cent. of phosphorus. Even after hardening in alcohol, it is dissolved completely by successive treatment with dilute acid and alkali. Heating with 1 per cent. sulphuric acid causes cleavage; the extract contains carbohydrate, phosphorised nitrogenous matter and bases, but neither proteid, protamine, nor nucleo-proteid. The decomposition products suggest that the cell is made up of nuclein or gluco-nucleo-proteid. Alcohol precipitates from the extract a hygroscopic toxic substance made up of sulphate, nucleic acid, and colon-toxin. No evidence of cellulose was found. By digestion with stronger acid, xanthine and hexone bases were obtained.

W. D. H.

A New Microbe which produces Acetone. L. BRÉAUDAT (*Compt. rend.*, 1906, 142, 1280—1282).—A chromogenic bacterium named *Bacillus violarius acetonicus* produces, when grown in peptone solution, acetone, among other substances. The bacterial origin of acetone in the body is considered to be a possibility.

W. D. H.

Quick-vinegar and Wine Vinegar Bacteria. WILHELM HENNEBERG (*Chem. Centr.*, 1906, i, 1796; from *Deutsche Essigindustrie*, 10, 89—93. Compare this vol., ii, 475).—The original paper con-

tains a description of five new vinegar bacteria and of *Bacterium xylinum*.

The new quick-vinegar bacteria, *B. Schützenbachii*, *B. curvum*, and *B. orleanense*, and the new wine-vinegar bacteria, *B. xylinoides*, which closely resembles *B. xylinum* and *B. vini acetati*, form acetic acid from arabinose, dextrose, erythritol, glycerol, and propyl alcohol, and, with the exception of *B. curvum*, also from lactose. Maltose is not converted into acid by *B. curvum* and *B. xylinum*, raffinose by *B. Schützenbachii* and *B. xylinoides*, or dextrin by *B. xylinoides*, but the other bacteria decompose these carbohydrates. Levulose is only attacked by *B. Schützenbachii* and *B. vini acetati*, sucrose by *B. xylinoides*, *B. xylinum*, and *B. vini acetati*, lactose by *B. Schützenbachii* and *B. orleanense*, and mannitol only by *B. orleanense* and *B. vini acetati*. The acid formed is again destroyed in the case of *B. xylinoides* and *B. xylinum* in dextrose solution, and of *B. xylinum* in solutions of sucrose and glycerol.

The vinegar bacteria are greatly affected by free acetic acid if present in large quantities at the beginning of the experiment. Quantities up to 15 per cent., however, have no effect, and the bacteria gradually become accustomed to the conditions. About 10 per cent. of alcohol appears to be the maximum quantity which the bacteria are able to withstand. In a factory experiment on a vinegar mash, the maximum quantity of acid formed by *B. Schützenbachii* was 10.9 per cent., by *B. xylinoides* 9.3, by *B. orleanense* 9, and by *B. vini acetati* 8. The vinegar produced by *B. xylinoides* and *B. orleanense* was frequently aromatic, and the former appeared to be able to form a large quantity of aldehyde under certain conditions. E. W. W.

Influence of High Sugar Concentration on the Work of Endotryptase in Dead Yeast Cells. T. GROMOFF (*Zeit. physiol. Chem.*, 1906, 48, 87—91).—In a former research, it was shown that solutions of sucrose up to 35 per cent. strength inhibited the autolysis of proteid. In the present investigation, strengths from 60 to 100 per cent. were employed, but the influence exerted was very small. Addition of ammonium tartrate to the sugar slightly favoured proteid decomposition. Potassium nitrate had no effect. W. D. H.

Influence of Metals on Fermenting Liquids. LEOPOLD NATHAN, ARTHUR SCHMID, and WILLY FUCHS (*Centr. Bakt. Par.*, 1906, ii, 16, 482—488. Compare *Abstr.*, 1905, ii, 340, 847).—The results of numerous experiments both with single metals and with two different metals together showed that tin is particularly injurious, and that tin and copper together are nearly as injurious as tin. It is considered probable that numerous failures and irregularities in fermentation are due to injurious metals having been employed. N. H. J. M.

Present Position of the Problem of the Chemical Sterilisation of Drinking Water. HETSCH (*Chem. Centr.*, 1906, i, 1671—1672; from *von Leuthold-Gedenkschrift*, 1906, 1).—The bacilli of cholera, dysentery, and typhus are not killed by the ferro-chlorine method when the largest quantities recommended by Duyk (*Ann. Chim.*

anal. 1903, 8, 13) are allowed to act for twenty minutes, and the water is not sterilised by the action of double these quantities for forty minutes. Experiments on the action of chlorine, made by adding liquid chlorine or pure chlorine water to infected water in sealed tubes, gave very variable results, but it was found that 234 mg. of chlorine per litre failed to kill typhus bacilli. It is probable, therefore, that much larger quantities of bleaching powder than Engels prescribed (*Centr. Bakt. Par.*, 1902, i, 32, 495), might prove ineffective.

Alkali fluorides are not suitable for the sterilisation of water. Two mg. of silver fluoride or Paternò and Cingolani's tachiol in 1 litre, killed cholera vibrios in thirty minutes, but not typhus bacilli; 5 mg. per litre killed cholera bacilli in ten minutes, and typhus and dysentery bacilli in twenty minutes. Water infected with spores was not sterilised by 5 mg. of silver fluoride in half an hour, and when agar culture was added 10 mg. of tachiol were also ineffective. The action of isotachiol (silver silicofluoride) was similar. Experiments on Freyssing and Roche's bicalcite method, which consists in adding calcium peroxide and a powder containing aluminium sulphate to the water and filtering, showed that the inventors' claim that nascent hydrogen peroxide is more active than ordinary hydrogen peroxide is not confirmed.

Complete sterilisation is only effected by silver fluoride or hydrogen peroxide when the infection has not passed a certain limit.

E. W. W.

Work of Respiration Enzymes of Plants under Different Conditions. WLADIMIR PALLADIN (*Zeit. physiol. Chem.*, 1906, 47, 407—451).—Comparing the amounts of carbon dioxide given off by frozen etiolated leaves in air and in hydrogen, it is seen that at first the anaërobic process predominates in both cases. In air, frozen leaves soon become black, whilst in hydrogen they retain their yellow colour the whole time.

When air is admitted to leaves kept in an atmosphere of hydrogen after the production of carbon dioxide has ceased, there is renewed production of carbon dioxide; the sum of the first and second amounts of carbon dioxide exceeds the amount given off by leaves kept in air from the commencement by 50 per cent., indicating that during anaërobic fermentation material is prepared for subsequent oxidation.

Etiolated leaves previously cultivated in sugar solutions yielded less carbon dioxide in hydrogen than leaves which had no sugar. The anaërobic production of carbon dioxide by frozen leaves has therefore nothing to do with alcoholic fermentation.

The carbon dioxide produced by leaves is due to the action of (1) carbonase, (2) oxydase, (3) oxygenase, and (4) peroxydase, the predominance of one or another depending on the degree of development of the plant. Anaërobic respiration predominates in the embryonal organs in which oxydase is almost completely absent.

N. H. J. M.

Action of Nitrites on Plants. ALBERT STUTZER (*J. Landw.*, 1906, 54, 125—138).—Nitrites act injuriously on germinating seeds.

Young sugar beet plants are especially sensitive, whilst red clover, at the end of the germinating period, resists the action of nitrites. Older, but not fully developed, plants are not injured.

The manurial value of nitrites is in some cases less, and in other cases greater, than that of nitrates.

N. H. J. M.

Composition and Metabolism of Seedlings. ERNST SCHULZE (*Zeit. physiol. Chem.*, 1906, 47, 507—569. Compare Abstr., 1903, ii, 566; 1904, ii, 836).—The following nitrogenous substances are produced in the breaking down of proteids during germination: aminovaleric acid, leucine, *isoleucine*, phenylalanine, tyrosine, tryptophan, α -pyrrolidine-2-carboxylic acid, arginine, lysine, histidine, asparagine, glutamine, and ammonia. It is probable that polypeptides also occur, and that alloxuric bases are produced by the breaking down of nuclein.

N. H. J. M.

Pigments of Diatom-Chromatophores. FRIEDRICH G. KOHL (*Chem. Centr.*, 1906, i, 1669; from *Ber. Deut. bot. Ges.*, 24, 124—134).—When the leather-yellow diatoms, *Achnanthisidium lanceolatum*, *Himantidium pectinale* var. *curta*, are treated with cold 70 per cent. alcohol for five minutes, carotin is extracted with only small quantities of chlorophyll and xanthophyll; on more prolonged treatment, however, larger quantities of the latter are extracted. The whole of the colouring matter may be removed by 96 per cent. alcohol at the ordinary temperature, and the solution then contains a large quantity of chlorophyll but very little carotin and xanthophyll. Molisch's leucocyanogen reaction is really caused by carotin in the case of diatoms, but is only produced by hydrochloric acid in alcoholic solution; xanthophyll is not affected. The change of colour of diatoms depends on the access of the solvent to the chromatophores. The alcohol kills the contents of the cell instantaneously and the carotin is at once dissolved, but not the chlorophyll; the colour changes to bluish-green. The colouring matter of diatoms is not different from that of the leaves of phanerogams. Diatomin does not exist and leucocyanogen is not contained in the diatoms examined. The change to brown, produced by potassium hydroxide on the chromatophores of leaves, is accompanied by a definite change in the absorption spectrum, the bands being displaced towards the violet. The chlorophyll contained in the living brown diatom chromatophores is spectroscopically identical with that which is present after the change of colour. The cause of the colour change is to be attributed to changes which render the colour of the chlorophyll more apparent. The change of colour in the case of the fucoxanthin of phycophaceæ may, however, be wholly or partly caused by carotin.

E. W. W.

Bark and Fruits of *Ægiceras Majus* with especial Reference to Saponin. H. WEISS (*Arch. Pharm.*, 1906, 244, 221—233).—The first part of the paper is of botanical interest.

From the bark, in addition to about 1 per cent. of saponin, a crystalline substance, $C_{22}H_{24}O_8$, was obtained by extraction with chloroform and subsequent purification; it melted at 83—84° and did not form an

acetyl derivative. The saponin $C_{66}H_{90}O_{12}(OH)_{18}$ yielded an amorphous acetyl derivative, $C_{102}H_{144}O_{48}$ (analysed, and molecular weight and saponification number determined); when hydrolysed with 2 per cent. sulphuric acid, it yields 20.4 per cent. of sapogenin, 13.0 of pentoses, and galactose.

The husks of the fruits do not contain saponin. From the kernels, on the contrary, a saponin was isolated identical chemically with that obtained from the bark; but physiologically ten times more powerful in its action on the red corpuscles of the blood. C. F. B.

Formation of Respiration Enzymes in Injured Bulbs of *Allium Cepa*. T. KRASNOSSELSKI (*Chem. Centr.*, 1906, i, 1622; from *Ber. Deut. bot. Ges.*, 24, 134—141).—Oxydases are not contained in injured or frozen bulbs of *Allium cepa* or their juices. The quantity of peroxydases increases with the energy of respiration, but when the latter begins to decrease the quantity of peroxydases still increases. The juice obtained from the frozen bulbs contains catalase. The respiration coefficients show that, immediately after thawing, the emission of carbon dioxide is greater than the absorption of oxygen, and that later the reverse is the case. E. W. W.

Fly Agaric (*Amanita Muscaria*). III. JULIUS ZELLNER (*Monatsh.*, 1906, 27, 281—293. Compare Abstr., 1904, ii, 678; 1905, ii, 550).—In addition to the substances previously isolated from the ethereal extract of the fungus, a calcium salt of a viscid acid, which resembles, but is not identical with, calcium malate, has now been obtained. Only traces of tannin were obtained.

The yellowish-red dye, which is thrown down together with the lead acetate precipitate, is readily soluble in water or alcohol; the aqueous solution is yellowish-red to deep red, has a slight green fluorescence, and forms precipitates with lead and copper acetates. The dye is not bleached by prolonged action of moist sulphur dioxide, and is oxidised only slowly by dilute chlorine water or chromic acid solution.

The filtrate from the precipitate formed with basic lead acetate contains choline, muscarine, mannitol, dextrose, and mycose.

As mannitol is obtained only in traces from the fresh fungus, but is present to the extent of 6—7 per cent. in the dried substance, it must be formed by the action of a ferment during the process of drying.

Dextrose is present only in traces in the young plant, but in large amounts in the mature fungus.

After extraction of the fats by means of light petroleum, 54 per cent. of the dried fungus dissolves in water. The aqueous extract contains proteids (albumins?), amorphous carbohydrates, amorphous nitrogenous substances the nature of which has not been determined, peptones, and xanthine.

Only small amounts of proteid are obtained from the dried substance, but larger amounts from the fresh fungus. Proteids may be extracted also by treatment of the fungus with 10 per cent. sodium chloride solution, or with dilute alkali hydroxides.

Boudier's viscosin (*Die Pilze*, 1867) is not a pure carbohydrate, as it contains nitrogenous compounds. The same author's mycetid is a

mixture of carbohydrates, consisting principally of a gum, together with viscosin, and a substance resembling dextrin.

In addition to the ferment which hydrolyses the fats and that which causes the formation of mannitol, the fungus contains a diastatic ferment to which are ascribed the changes which take place on drying the substance.

Fungin (fungus cellulose) also is present.

G. Y.

Composition of Lemon Juice. ADOLF BEYTHIEN, PAUL BOHRISCH, and HANS HEMPEL (*Zeit. Nahr. Genussm.*, 1906, 11, 651—661).—The following average results were obtained on the analysis of nine samples of lemon juice pressed from fruit grown in the year 1905: total citric acid, 5.717; total sugar (as invert sugar), 0.119; ash, 0.463 per cent.; alkalinity of ash, 5.820 c.c. *N/1* acid. Nine samples of commercial juice made in 1905 yielded (average): total citric acid, 5.959; total sugar, 0.743; ash, 0.402 per cent.; alkalinity of ash, 5.075 c.c. *N/1* acid.

W. P. S.

Composition of Lemon Juice. VON KÜTTNER and ULRICH (*Zeit. öffentl. Chem.*, 1906, 12, 202—211).—The results are recorded of the analyses of thirty-seven samples of commercial lemon juice and of seventeen samples of juice pressed from the fruit by the authors themselves. The quantity of ash given by the first set of samples varied from 0.2200 to 0.6380 per cent., the alkalinity of the ash corresponding with from 2.25 to 6.50 c.c. of *N/1* acid per cent. In the second series of samples, the ash varied from 0.222 to 0.485 per cent. and the alkalinity of the ash from 3.40 to 5.20 c.c. of *N/1* acid. Attention is drawn to the fact that lemon juice may be preserved by the addition of from 0.1 to 0.4 per cent. of formic acid. This quantity is sufficient to prevent the juice being spoiled by the formation of acetic acid.

W. P. S.

The Seeds and Oil of Mountain Ash Berries. LEOPOLD VAN ITALIE and C. H. NIEUWLAND (*Arch. Pharm.*, 1906, 244, 164).—When freed from oil, the seeds contained water, 9.2; nitrogen, 5.4; cellulose, 13.2; ash, 5.2; carbohydrate (as dextrose), 24.2; hydrocyanic acid, 0.00073 per cent.

The oil, which was extracted with light petroleum, forms 22 per cent. of the seeds; it is mobile, pale yellowish-brown in colour, and sweet in taste; it dries rapidly in the air. It has a sp. gr., 0.9317 at 15°, n_D^{15} 1.4753 at 15°; acid number, 2.35; saponification number, 208; iodine number, 128.5; the fatty acid obtained from it has acid number, 230.2; iodine number, 137.5.

C. F. B.

Growth and Ripening of Persimmons. WILLARD D. BIGELOW, HERBERT C. GORE, and B. J. HOWARD (*J. Amer. Chem. Soc.*, 1906, 28, 688—703).—A study has been made of the changes which occur during the ripening of persimmons, this fruit having been specially selected since it contains a relatively large amount of tannin. Both the wild persimmon (*Diospyros Virginiana*) and the Japanese persimmon (*Diospyros Kaki*) have been investigated. Samples were collected at

various stages of growth, and estimations were made of the proportions of pulp, seed, and calyx in the fruits and of the total solids (dried at 70° under 100—200 mm. pressure), marc (the portion of the flesh insoluble in 95 per cent. alcohol), acids (calculated as H_2SO_4), reducing sugars, soluble tannin, total nitrogen, soluble nitrogen, and ash. Analyses were made both of fresh persimmons and also of fruits which had been stored for periods varying from five to twenty-five days. The results are tabulated and plotted as curves.

It is found that during the ripening of the fruit as the weight of the pulp increases, the total determined solids, sugar, and marc also increase. The tannin, however, decreases somewhat rapidly as the marc increases. After full maturity has been attained, a diminution takes place in the reducing sugars and soluble solids. During ripening in storage, a loss occurs in total solids, determined solids, and sugar, whilst a large increase takes place in marc and a corresponding decrease in tannin.

A number of possibilities are discussed to account for the disappearance of the tannin during the ripening, and the conclusion is drawn that this substance either combines with some constituent of the undetermined solids of low molecular weight, or is converted into an insoluble form by a change in its own nature.

A microscopical study has been made of the fruit. The results show that the tannin is at first diffused fairly uniformly through the fruit, but that, as ripening takes place, it becomes deposited in an insoluble form in certain specialised cells. The paper is illustrated with microphotographs.

E. G.

Quantity of Iron contained in Spinach. H. SERGER (*Chem. Centr.*, 1906, i, 1668; from *Pharm. Zeit.*, 51, 372).—Four samples of winter spinach contained 86.70—89.50 per cent. of water, and 9.58—13.30 of combustible substances; they yielded 1.9077—3.1088 per cent. of ash. One hundred grams of dry substance contained an average of 0.104 gram of iron. From 100 grams of fresh winter spinach, dilute alcohol extracted 4.3 grams of substances which contained 0.179 per cent. of iron and gave 26.23 per cent. of ash; the residual material yielded 8.7 grams of dry substance which contained 0.0656 per cent. of iron, and gave 9.18 per cent. of ash. A mixture of benzene, chloroform, and ether extracted 1.60 per cent. of substances which contained 0.189 per cent. of iron, and yielded 19.78 of ash. *Spinol sicc.*, or "Stroschein," and *Extr. Ramkulini*, gave 31.45 and 44.47 per cent. of ash, and contained 0.257 and 2.00 per cent. of iron respectively.

E. W. W.

Assimilation and Distribution of Silica and Potassium in Tobacco Plants. EDWIN BLANCK (*Landw. Versuchs-Stat.*, 1906, 64, 243—248).—Pot experiments are described in which tobacco was manured with potassium in the form of (1) martellin, (2) humus-silica, and (3) potassium sulphate. The greatest yield was obtained with martellin, and the lowest with potassium sulphate. The martellin plants contained the most silica and potassium, the humus-silica plants the least potassium, and the potassium sulphate plants

the least silica. The amounts of silica and potassium in the different parts of the plants are given.

N. H. J. M.

Composition of Tomatoes and Tomato Juice. W. STÜBER (*Zeit. Nahr. Genussm.*, 1906, 11, 578—581).—The following percentage results were obtained on the analysis of two samples of tomatoes and the juices expressed from the same :

	Fruit 1.	Fruit 2.	Juice 1.	Juice 2.
Water	94.52	95.13	96.00	96.19
Nitrogen	0.116	0.159	0.098	0.088
Ash	0.50	0.63	0.50	0.63
Alkalinity of ash (c.c. <i>N</i> -acid)...	4.62	5.50	5.20	6.20
Light petroleum extract	0.06	0.07	—	—
Total sugars (after inversion)...	2.51	3.19	2.34	1.96
Acidity (as citric acid)	0.41	0.48	0.60	0.69
Phosphoric acid	0.044	0.059	0.031	0.039

The acidity consisted principally of citric acid. Tartaric, malic, and succinic acids could not be detected in the samples.

W. P. S.

Injurious Effect of Calcium Carbonate on Bog Moss. H. PAUL (*Chem. Centr.*, 1906, i, 1799 ; from *Ber. Deut. bot. Ges.*, 24, 148—154).—The *Sphagnaceæ* are very sensitive to the action of solutions of calcium carbonate (prepared by passing carbon dioxide into water). The maximum quantity which is not fatal varies from 77 to 312 mg. CaCO_3 per litre, according to the kind of moss. Whilst the moss is not injured by the presence of comparatively large quantities of gypsum and some potassium salts, extremely small quantities of many phosphorus compounds are deleterious.

The red dye from *Sphagnum rubellum* turns blue in the presence of an injurious quantity of calcium carbonate. The dye behaves like red litmus, and is a sensitive indicator for alkalis.

E. W. W.

Absorption of Potassium by Soils. OSWALD SCHREINER and GEORGE H. FAIRYER (*J. Physical Chem.*, 1906, 10, 361—369).—Experiments were made on the absorption of potassium salts by the soils previously used in similar experiments with phosphates (this vol., ii, 485). The general nature of the results both for the absorption and the subsequent removal of the salts by water was quite similar to what was found in the case of the phosphates.

L. M. J.

Experiments with New Nitrogenous Manures. JOHN SEBELIEN (*J. Landw.*, 1906, 54, 159—185).—Basic calcium nitrate (a mixture of calcium nitrate with an excess of lime) gave sometimes less and sometimes greater yields than corresponding amounts of sodium nitrate. The better results with the calcium salt are sometimes, but not always, due to the calcium, and in such cases sodium nitrate in conjunction with calcium carbonate gives the same results as calcium nitrate.

Field experiments with cereals, in which sodium nitrate, calcium nitrate, ammonium sulphate, and calcium cyanamide were compared,

showed that on *Sphagnum* peat-soil calcium nitrate gave results equal to those obtained with sodium nitrate, whilst calcium cyanamide had very little effect at all, or was even injurious. The results of grass experiments in different parts of Norway showed that sodium and calcium nitrates were equal in value; whilst calcium cyanamide gave considerably less increase of yield.
N. H. J. M.

Substitution of Potassium by Sodium in Sugar-beet.
JOSEF URBAN (*Zeit. Zuckerind. Böhm.*, 1906, 30, 397—402).—The composition of the ash of sugar-beet leaves and roots varies according to the soil and the action of manure, &c. Considerable amounts of sodium salts may be taken up, the amount of sodium sometimes exceeding that of potassium. The latter cannot, however, be replaced with respect to its action on the production of sugar. To obtain a high percentage of sugar there should be a definite relation between the potassium and nitrogen, about 1:1. When nitrogen is greatly in excess of the potassium, leaf production is greatly increased, and there is an excess of leaf over root.
N. H. J. M.

Analytical Chemistry.

Report on Graduated Vessels at the Sixth International Congress for Applied Chemistry at Rome, 1906. HEINRICH GÖCKEL (*Chem. Centr.*, 1906, i, 1589—1590; from *Zeit. chem. Apparatenkunde*, 1, 305—315).—The author proposes various changes in the recommendations of Commission III of the International Analysis Commission in reference to apparatus for volumetric and gas analysis. For details, the abstract or original paper should be consulted.

E. W. W.

Modification of Maquenne's Wash-bottle. ANTOINE VILLIERS (*Ann. Chim. anal.*, 1906, 11, 211).—Maquenne's washing contrivance (*ibid.*, 167) has been improved by the introduction of a bulb on the entering tube so as to prevent regurgitation and thus to render the apparatus applicable to the absorption of carbon dioxide in combustions in a closed tube.

L. DE K.

Preservation of Standardised Liquids. FRANZ RESCH (*Chem. Centr.*, 1906, 1, 1389—1390; from *Zeit. Oesterr. Apoth. Ver.*, 44, 159—160).—An arrangement by which the standard liquid in the reservoirs remains unaltered. The air entering the apparatus is purified by passing it over potassium hydroxide, calcium chloride, and sulphuric acid. The liquid comes into contact with glass only, and the burette-stand can be dispensed with. For particulars, the illustrations in the original should be consulted.

L. DE K.

Standardisation of Iodine and Thiosulphate Solutions.

GUSTAV BRUHNS (*Zeit. anorg. Chem.*, 1906, 49, 277—283. Compare Metzl, this vol., ii, 194).—Topf, and following him Metzl (*loc. cit.*), on the basis of results obtained by Zulkowsky, have expressed the view that the reaction between potassium iodide and potassium dichromate in acid solution is incomplete, but the author points out that Zulkowsky's observations in this connection have been misunderstood and shows, from the results obtained by the latter, and by experiments of his own, that the dichromate is completely reduced, even in dilute solution, if the mixture is left for a short time before the thiosulphate is added. The conditions necessary for obtaining accurate results by this method are fully discussed; it is shown that the end point is sharper when a fair excess of hydrochloric acid is used.

Potassium permanganate may advantageously be substituted for the dichromate in standardising thiosulphate solutions as the reaction is practically instantaneous, and it is easy to judge from the appearance of the mixture when sufficient potassium iodide and acid have been added. Contrary to the general opinion, permanganate solutions are perfectly stable when the traces of organic matter in the distilled water used as solvent have been oxidised. G. S.

Antimonyl Potassium Tartrate as a Standard for Iodimetry.

OSKAR LUTZ (*Zeit. anorg. Chem.*, 1906, 49, 338—340. Compare Metzl, this vol., ii, 194).—A discussion of some points raised by Metzl in his recent paper on the same subject. G. S.

Application of Sodium Hyposulphite in Gas Analysis.

HARTWIG FRANZEN (*Ber.*, 1906, 39, 2069—2071).—An alkaline solution containing 50 grams of sodium hyposulphite in 250 c.c. of water completely absorbs the oxygen in a gaseous mixture in five minutes, provided that the concentration of the oxygen is not too great. The reaction is represented by the equation $\text{Na}_2\text{S}_2\text{O}_4 + \text{H}_2\text{O} + \text{O} = 2\text{NaHSO}_3$. The solution has the advantage over other oxygen absorbents in that it is only slightly alkaline, works efficiently at low temperatures, and does not absorb carbon monoxide. C. S.

Use of Ozone in Quantitative Analysis. PAUL JANNASCH and WILLY GOTTSCHALK (*J. pr. Chem.*, 1906, [ii], 73, 497—519. Compare Abstr., 1904, ii, 782).—A convenient form of ozone generator is figured and described.

Precipitates are obtained on passing a current of ozone through aqueous solutions of cobalt, silver, lead, manganese, and bismuth salts, the last in presence of an alkali hydroxide. Manganese tetroxide is precipitated quantitatively if a solution of a manganese salt is dropped into concentrated ammonia solution through which is passed a rapid current of ozone. The quantitative separation of manganese from sodium, magnesium, calcium, nickel, zinc, cadmium, and copper by precipitation of manganese in this manner is described; the other metals present are estimated in the filtrate. To complete the separation from magnesium, nickel, cadmium, and copper, the manganese tetroxide is dissolved in hydrochloric acid containing hydrogen peroxide and the precipitation repeated. G. Y.

Volumetric [Iodometric] Estimation of Combined Sulphuric Acid. FERNAND TELLE (*J. Pharm. Chim.*, 1906, [vi], 23, 573—574).—A reply to Scholtz (this vol., ii, 195), in which the author claims priority.
L. DE K.

Estimation of Hyposulphurous Acid in Hyposulphites and their Compounds with Formaldehyde. ALPHONSE SEYEWETZ and BLOCH (*Bull. Soc. chim.*, 1906, [iii], 35, 293—297).—When an aqueous solution of an alkali hyposulphite is added to a solution of silver chloride in ammonia, the chloride is reduced quantitatively in the cold, a precipitate of metallic silver being formed. This process may be used for the estimation of hyposulphites, the precipitated silver being weighed. In the case of the formaldehyde compound of sodium hyposulphite (compare Baumann, Thesmar, and Frossard, *Abstr.*, 1905, i, 260), its aqueous solution must be added to excess of the ammoniacal solution of silver chloride and the mixture boiled for about four minutes, as reduction in this case is incomplete below 80°.

T. A. H.

Simplified Method for the Estimation of Nitric Acid in Nitrates. J. TH. BORNWATER (*Chem. Centr.*, 1906, i, 703; from *Chem. Weekblad.*, 3, 30—31).—0.5 gram of the nitrate is introduced into an 800 c.c. Erlenmeyer distilling flask and dissolved in 200 c.c. of water. The flask is fitted with a long, vertical bulb-tube, the top of which is bent and connected with a vertical condenser. Five c.c. of alcohol, 50 c.c. of aqueous potassium hydroxide of sp. gr. 1.3, and 2.5 grams of small pieces of aluminium wire are added, and the whole is heated gently until evolution of gas ceases. The ammonia formed is then boiled off and collected in standard acid.
L. DE K.

Detection of Nitrates in Alkali Iodides. E. BARONI (*Chem. Centr.*, 1906, i, 1714; from *Giorn. Farm. Chim.*, 55, 152—154).—One gram of the suspected sample, which should be free from iodate, is added to 20 c.c. of a 5 per cent. mercuric chloride solution and the filtrate is strongly acidified with sulphuric acid. When cold, the liquid is tested in the usual manner for nitric acid by means of a solution of ferrous sulphate. The ring is still visible with 0.01 per cent. of nitrate. Another portion of the liquid may be tested also with diphenylamine in presence of sulphuric acid.
L. DE K.

A Qualitative Test for Phosphorus. PAUL MAURICHEAU-BAUPRÉ (*Compt. rend.*, 1906, 142, [xxii], 1206—1207).—If hydrogen or acetylene containing hydrogen phosphide is burnt in a Bunsen burner, the products of combustion will contain phosphoric acid. If now a piece of glass attached to a platinum wire is held just in the top of the flame for a few minutes, the glass will become corroded and slightly increase in weight. This reaction may therefore serve to detect phosphorus in iron, for instance.

Phosphorus in volatile phosphates or in organic substances such as yolk of egg may be determined by burning some of the substance on a platinum wire in a burner fed with hydrogen or pure acetylene, holding the wire just underneath the piece of glass.
L. DE K.

New Modification of the Estimation of Phosphoric Acid by Precipitation as Magnesium Ammonium Phosphate, particularly in Regard to Manures. GUNNER JÖRGENSEN (*Zeit. anal. Chem.*, 1906, 45, 273—315).—A lengthy article unsuitable for adequate abstraction. The novel point is that the precipitation with magnesium mixture (with or without citric acid) is effected at the boiling temperature.
L. DE K.

Application of Compressed Air in Superphosphate Analysis. GEORG SCHLIEBS (*Chem. Zeit.*, 1900, 30, 584).—Twenty to forty grams of the sample are mixed with 700 c.c. of water in a two-litre flask, and by means of a glass tube reaching to the bottom a current of compressed air is passed for half an hour. As soon as the liquid has attained the temperature of the room, the contents of the flask are diluted to the mark and the analysis is proceeded with in the usual manner.
L. DE K.

A Characteristic Reaction for Borax. C. REICHARD (*Chem. Centr.*, 1906, i, 1714; from *Pharm. Zeit.*, 51, 298—299).—A mixture of borax and α -nitroso- β -naphthol, when moistened with cold water, turns a bright green. This test is characteristic for ordinary borax, for an excess of boric acid prevents the reaction.
L. DE K.

Decomposition of Silicates with Hydrofluoric and Hydrochloric Acids. FRITZ HINDEN (*Zeit. anal. Chem.*, 1906, 45, 332—342).—One gram of the silicate, reduced to an impalpable powder, is placed in a platinum dish, moistened with a few drops of water, and mixed with about 15 c.c. of hydrofluoric acid. The whole is evaporated to dryness on the water-bath, and after adding 10 c.c. of dilute hydrochloric acid (1:1) the solution is again evaporated to dryness with addition of another 10 c.c. of hydrofluoric acid. The residue, consisting of fluorides and silicofluorides, is now converted completely into chlorides by evaporating some six times in succession with 20 c.c. of dilute hydrochloric acid. The various salts are then separated by the usual methods. Sodium and potassium fluorides may also be converted into chlorides by ignition with ammonium chloride.
L. DE K.

Separation of Silicic Acid when Estimating Citrate-soluble Phosphoric Acid. JULIUS HASENBÄUMER (*Chem. Zeit.*, 1906, 30, 665—666).—A series of experiments from which it appears probable that the higher results obtained without previous separation of silica are caused by the fact that separated gelatinous silica retains phosphoric acid.

It is suggested that the composition of the magnesium phosphate may differ slightly and that this depends on the presence of silica in the solution.
L. DE K.

Sampling of Coal and Classification of Analytical Data. A. BEMENT (*J. Amer. Chem. Soc.*, 1906, 28, 632—639).—The paper

deals with the importance of selecting a thoroughly representative sample for analysis.

The word "combustible" used to designate a fuel free from ash and moisture is, in the author's opinion, erroneous and the expression "pure coal" is proposed instead.

L. DE K.

Estimation of Carbonic Acid. WILHELM HOLTSCHMIDT (*Chem. Zeit.*, 1906, 30, 621—625).—The improvement consists in the use of potassium hydrogen tartrate, which on prolonged boiling completely expels the carbon dioxide. This is then absorbed in barium hydroxide solution and determined volumetrically, or absorbed in a weighed soda lime-tube and determined gravimetrically.

The operation, on account of the large quantity of water condensed, requires a special apparatus, for a description of which the illustrations in the original article should be consulted.

L. DE K.

Apparatus for Testing Saturation and Boiler-Gases. ALFRED SALOMON (*Chem. Zeit.*, 1906, 30, 638—639).—An improvement in the Stammer tube, an apparatus much used for the examination of gaseous matters in sugar refineries. Carbon dioxide is, as usual, found by measuring the gas before and after contact with potassium hydroxide. For full description, the drawing in the original should be consulted.

L. DE K.

Estimation of Carbon Disulphide in Benzene. D. STAVORINUS (*Chem. Centr.*, 1906, i, 705; from *J. Gasbel.*, 49, 8).—Twenty-five c.c. of the sample are mixed with 70 c.c. of 96 per cent. alcohol and 10 c.c. of 2*N* sodium hydroxide. After half an hour, 5 c.c. of concentrated hydrogen peroxide are added, the alcohol is removed by evaporation, and the sulphate formed is estimated as usual.

The method may also be applied volumetrically by using 10 c.c. of *N*-alkali and titrating the excess with *N*/5 acid, using methyl-orange as indicator. One c.c. *N*/5 alkali = 0.019 gram of carbon disulphide.

L. DE K.

Estimation of Potassium in Potassium Salts and Mixed Manures by Neubauer's Modified Finkener's Method. MAX KLING and OTTO ENGELS (*Zeit. anal. Chem.*, 1906, 45, 315—332).—The authors approve, on the whole, of the process proposed by Finkener and modified by Neubauer. In this process, the excess of platinic chloride is removed by alcohol and the residue ignited in a current of coal gas. The metallic platinum is washed first with boiling water and then with hot dilute nitric acid, ignited, and weighed.

Ammonium salts and earthy phosphates must be removed previously by the ordinary methods.

When operating on 0.5 gram of material, the percentage of potassium oxide is found by multiplying the weight of the reduced platinum by 0.48108. A convenient table for saving calculation is appended.

L. DE K.

Estimation of Cadmium. CARL GOLDSCHMIDT (*Zeit. anal. Chem.*, 1906, 45, 344).—Cadmium is precipitated quantitatively by boiling its solutions in an aluminium vessel in presence of a trace of chromium nitrate and cobalt nitrate. Aluminium is the catalyst. The case resembles that of the precipitation of gold by nickel or silver by cobalt.
L. DE K.

Estimation of Lead. OTTO MAYER (*Chem. Centr.*, 1906, 1, 1715; from *Pharm. Zeit.*, 51, 299).—The lead solution containing some free acetic acid is precipitated while hot with slight excess of standard potassium dichromate, and the precipitate is washed with 50 c.c. of 1 per cent. acetic acid. The excess of dichromate is then estimated iodometrically as usual.
L. DE K.

Volumetric Estimation of Lead. OTTO SASSE (*Chem. Centr.*, 1906, 1, 1715; from *Pharm. Zeit.*, 51, 341).—The author states that he estimated lead volumetrically some seventeen years ago by the process now communicated by Mayer (see preceding abstract).
L. DE K.

Estimation of Lead in Alloys of Tin and Lead. G. GIUSTI (*Chem. Centr.*, 1906, 1, 1462—1463; from *Staz. sperim. agrar. ital.*, 38, 820—831).—Within certain limits the percentage of lead may be calculated with sufficient accuracy from the sp. gr. of the sample, tin having a sp. gr. of 7.29 and lead of 11.44.
L. DE K.

Assay of Babbit Metal. H. YOCKEY (*J. Amer. Chem. Soc.*, 1906, 28, 646—648).—One gram of the metal is heated with 20 c.c. of dilute nitric acid (1:2) in a covered beaker and finally evaporated to dryness. After heating for an hour at 120°, the mass is moistened with nitric acid and boiled with 40 c.c. of water. The mixed oxides of tin and antimony are collected, washed, ignited, and weighed. The filtrate is diluted to 250 c.c. and 50 c.c. are mixed with 10 c.c. of dilute ammonia (1:1) and 6 c.c. of glacial acetic acid. The liquid is heated to boiling and the lead is titrated with standard solution of ammonium molybdate (1 c.c. = 0.01 gram of lead) using tannic acid as indicator. To the other 200 c.c. is added sodium carbonate until a precipitate forms and then 2 c.c. of ammonia. Any copper is then titrated with standard potassium cyanide.

Another gram of the metal is then boiled with 1 gram of potassium iodide, 40 c.c. of fuming hydrochloric acid, and 40 c.c. of water. The metallic antimony is collected on a tared filter, washed first with hot dilute acid (1:10), then with hot water, and finally with alcohol. Its weight is calculated into the oxide, which is then deducted from the joint oxides of antimony and tin.
L. DE K.

Electrolytic Estimation of Mercury, using the Rotating Anode. GUSTAV KROUPA (*Chem. Centr.*, 1906, i, 705; from *Oesterr. Zeit. Berg. Hütt.*, 54, 26—27).—Winkler first proposed the extraction of mercury ores with sodium sulphide. From this solution the metal

may be deposited quantitatively by electrolysis, using a rotating anode, but the operation takes about one hour and a half. In that time, however, an experienced operator may perform ten mercury determinations by the Eschka process. L. DE K.

Estimation of Talc. R. KRZÍŽAN (*Zeit. Nahr. Genussm.*, 1906, 11, 641—650).—The estimation of talc on rice, pearl barley, &c. (the mineral being added to give the grains a glistening coat), is best carried out by heating the grains with hydrogen peroxide and ammonia. Minute bubbles of gas are formed between the skin of the grains and the talc coating and completely remove the latter. The liquid is then decanted, the grains are shaken and washed several times with water, and the total liquid obtained is boiled after the addition of a little hydrochloric acid and chromic acid. This oxidises most of the organic matter present. The solution is then filtered and the residue ignited at the lowest possible temperature. The weight of the ash will give the amount of talc present on the quantity of grain taken for the estimation. Owing to the solubility of the mineral in hydrochloric acid and to its varying composition, methods depending on the estimation of the magnesia in the portion of the ash which is insoluble in hydrochloric acid are quite untrustworthy. W. P. S.

Iron in Living Tissues. ANTOINE MOUNEYRAT (*Compt. rend.*, 1906, 142, 1572—1573. Compare this vol., ii, 495).—A method is described, which avoids accidental contamination with the metal consisting essentially in the use of platinum utensils, and reagents free from iron, for obtaining the iron of the tissues. W. D. H.

Estimation of Small Quantities of Iron. W. MCKIM MARRIOTT and CHARLES G. L. WOLF (*J. Biol. Chem.*, 1906, 1, 451—461).—The method employed is a colorimetric one with thiocyanate in the presence of acetone, which renders the reaction much more sensitive and applicable to the detection of the small amount of iron in animal fluids and tissues. W. D. H.

Sources of Error in the Titration of Iron with Permanganate. H. KINDER (*Chem. Zeit.*, 1906, 30, 631—632).—The use of ferrous ammonium sulphate or electrolytically precipitated iron for the standardisation of permanganate is attended with slight sources of error on account of possible impurities in these substances.

Good results are obtained by standardising with a pure iron of known composition, the amount being found by determining the various impurities and thus estimating the iron by difference; a trace of copper, however, counts as iron.

In the titration process, when the iron is reduced to the ferrous state by means of stannous chloride, the excess of which is then removed with mercuric chloride, it is of great importance to wait for some twenty-five seconds before commencing the titration, as otherwise the reduction of the mercury may not be complete. L. DE K.

Estimation of Antimony in Vulcanised Indiarubber. B. WAGNER (*Chem. Zeit.*, 1906, 30, 638).—0.5–1 gram of the finely-divided material is mixed in a porcelain crucible with five times its weight of a mixture of 1 part of sodium nitrite and 4 parts of potassium carbonate, and a little more of the oxidising mixture is sprinkled over the top. The whole is heated, cautiously at first, then gradually more strongly until at last the mass commences to fuse. If unburnt carbonaceous particles are noticed, these are easily oxidised by addition of a little nitre and heating in a covered crucible.

The mass is dissolved in water and boiled with excess of hydrochloric acid to expel nitrous fumes, the solution is filtered and then precipitated hot with hydrogen sulphide. The precipitated antimony sulphide, which in presence of other metals should be dissolved in ammonium sulphide and reprecipitated by hydrochloric acid, is collected on a weighed asbestos filter, heated in a current of dry carbon dioxide, and weighed as antimonious sulphide. L. DE K.

Qualitative Detection of Gold and Platinum in Inorganic Analysis. JULIUS PETERSEN (*Zeit. anal. Chem.*, 1906, 45, 342–344).—Into the slightly acid and warm solution of the metals is introduced an excess of zinc cuttings, which in the course of about fifteen minutes precipitated mercury, silver, lead, bismuth, copper, cadmium, platinum, gold, arsenic (of which the bulk, however, volatilises as hydride), antimony, tin, and a portion of the cobalt and nickel.

The metallic deposit is washed and treated with dilute hydrochloric acid, which dissolves the excess of zinc, also cadmium, tin, and some cobalt. After thorough washing, the residue is boiled with dilute nitric acid, which dissolves mercury, lead, bismuth, cobalt, and nickel, leaving gold and platinum and antimony oxides undissolved. These are then mixed with some solid ammonium nitrate and chloride, and heated in a porcelain crucible. The antimony volatilises completely as chloride, and the residue is then dissolved in a few drops of *aqua regia*. One-half of the solution is tested for platinum with ammonium chloride, and the other portion for gold with sulphurous acid, or an alkaline solution of hydrogen peroxide. L. DE K.

Apparatus for Sampling Waters. SPITTA and IMHOFF (*Chem. Centr.*, 1906, i, 591; from *Mitt. K. Prüfungsanstalt Wasservers. Abwassertechnik*, 6, 75–87).—Improved apparatus for taking samples of water at any desired depth. All danger of contact with atmospheric air is avoided. L. DE K.

Electrical Elementary Analysis. FRITZ VON KONEK (*Ber.*, 1906, 39, 2263–2265).—The author advocates the use of the Heraeus furnace for combustions, not only of substances which are readily volatile, but also for substances which burn with difficulty.

A. McK.

Estimation of Petroleum, Petrol Distillates, and Benzene in Oil of Turpentine, Oil of Pine, and Turpentine Substitutes. RICHARD BÖHME (*Chem. Zeit.*, 1906, 30, 633–635).—An improved

method for the estimation of petroleum, &c., in turpentine by means of sulphuric acid. It appears that fuming sulphuric acid is too strong, whilst the commercial acid is too weak for the purpose of dissolving oil of turpentine. The following process is therefore recommended.

Twenty c.c. of acid composed of 1 vol. of fuming and 3 vols. of ordinary sulphuric acid are put into a 40 c.c. flask, the neck of which holds 10 c.c. and is graduated to 0.2 c.c. Ten c.c. of the sample are added slowly (cooling if necessary) and the mixture is allowed to remain for one hour in the closed flask. The flask is then filled with ordinary sulphuric acid by running this carefully along the sides of the neck, and after about five hours the volume of the top layer is read off. This may then be used for chemical and physical tests. For further particulars, the exhaustive table in the original paper should be consulted.

L. DE K.

Examination of Oil of Turpentine. FRANZ UTZ (*Chem. Rev. Fett. Harz. Ind.*, 1906, 13, 161—163).—Results of estimations are given which show that the bromine absorption value (Abstr., 1906, ii, 310) is of little use in determining the purity of samples of oil of turpentine. Some resin oils have a bromine value sufficiently high to admit of their addition to oil of turpentine to the extent of 50 per cent. without decreasing the bromine value of the mixture below that of certain genuine oils. At the best, the bromine value simply indicates the amount of pinene in a sample.

W. P. S.

Estimation of Total Soluble Bitumen in Paving Material. SAMUEL AVERY and E. CORR (*J. Amer. Chem. Soc.*, 1906, 28, 648—654).—The authors having tried the various methods proposed from time to time, recommend the following method. A capsule prepared from hardened filter paper, is thoroughly extracted with carbon disulphide, dried for half an hour at 110°, and weighed in a closed tube. A weighed portion of the sample is placed in the paper and extracted with carbon disulphide in a Soxhlet tube. The residue is dried at 110° and reweighed. As, however, a small portion of the mineral matter invariably passes into the liquid, this should be evaporated to dryness and burnt to ash, and the weight of this added to that of the main residue.

The bitumen is thus found by difference.

L. DE K.

Estimation of Alcohol in Chloroform. MAURICE NICLOUX (*Bull. Soc. chim.*, 1906, [iii], 35, 321—335).—The alcohol is washed out by shaking 5 c.c. of the chloroform with 20 c.c. of water, the latter being then run off and the alcohol in it estimated colorimetrically with potassium dichromate by the process previously described by the author (Abstr., 1897, ii, 193; 1898, ii, 543).

T. A. H.

Estimation of Higher Alcohols in Spirits. II. PHILIP SCHIDROWITZ and FREDERICK KAYE (*Analyst*, 1906, 31, 181—194).—The results of further experiments with the Allen-Marquardt process (Abstr., 1905, ii, 486) are given which indicate that the process as a

whole gives very trustworthy results when the quantity of higher alcohols is not higher than 0.15 per cent. If more is found, the estimation should be repeated after diluting the spirit with pure 50 per cent. alcohol. It is shown that the result of the preliminary titration for "mineral acid" may be neglected when the figure obtained is less than one-tenth of the whole. The acidity usually reckoned as mineral acid is probably due in part to organic acids, as the quantity of chlorine present is not equivalent to the hydrochloric acid calculated from the titration. The colorimetric (sulphuric acid) process for the estimation of higher alcohols is shown to be quite untrustworthy.

W. P. S.

Tests for the Purity of [Commercial] Glycerol. OTTO SCHMATOLLA (*Chem. Centr.*, 1906, i, 1761—1762; from *Pharm. Zeit.*, 51, 363).—In addition to the German official silver tests, the following tests are recommended. Five c.c. of the sample are diluted with 5 c.c. of water, and 5 drops of solution of phenolphthalein and 1 drop of lime water are added; this should cause a red coloration persistent for a few minutes. If instead of phenolphthalein 1 drop of a 1 per cent. congo-red solution is added, 1 drop of *N*/10 hydrochloric acid should affect the colour. Metals are tested for with hydrogen sulphide or with solution of tannin (for iron only). Refined glycerol may be distinguished from the distilled article by generally containing more than 0.1 per cent. of mineral matter.

L. DE K.

Analysis of Gelatin Dynamites. THOMAS B. STILLMAN and PETER T. AUSTIN (*Bull. Soc. chim.*, 1906, [iii], 35, 373—376. Compare Smith, *Abstr.*, 1899, ii, 528).—A tabular plan of analysis for the examination of gelatin dynamites is given, depending on the successive extraction of the various constituents by suitable solvents. For details, the original must be consulted.

T. A. H.

Copper Solutions [for Sugar Estimations]. HENRI PELLET (*Chem. Centr.*, 1906, i, 702; from *Bull. Assoc. Chim. Sucre. Dist.*, 23, 535—537).—The proposal recently made by Lavalle (*Abstr.*, 1905, ii, 558) to prevent the precipitation of cuprous oxide by adding a large excess of alkali, is not novel and cannot be recommended. The best Fehling and similar copper solutions are obtained when the copper sulphate and the other materials are dissolved and kept separately; this fact does not seem to be sufficiently appreciated, at least in France.

L. DE K.

Differentiation between the various Sugars in Urine. FRIEDRICH ESCHBAUM (*Chem. Centr.*, 1906, i, 1763—1764; from *Apoth. Zeit.*, 21, 330—331).—The reduction test shows dextrose, lævulose, lactose, pentose, and the conjugated glycuronic acids, the osazone test only works with dextrose, lævulose, and pentose, whilst the fermentation test only gives decided results with dextrose and lævulose, as lactose fermentation only sets in after twenty-four hours. Dextrose and lactose polarise to the right, whilst the lævulose and the conjugated glycuronic acids show left-handed polarisation.

The orcinol test for pentose is carried out as follows: 0.03 gram of powdered orcinol is dissolved in 10 c.c. of fuming hydrochloric acid, and a drop of dilute ferric chloride is added. Of this reagent, 5 c.c. are put into a test-tube with 2 c.c. of the urine to be tested, the tube is closed with a plug of cotton-wool, and the mixture heated nearly to boiling. In the presence of pentose, an emerald-green coloration appears gradually, and soon becomes dark green. L. DE K.

Estimation of Diabetic Sugar in Urine by Fermentation. F. GOLDMANN (*Chem. Centr.*, 1906, i, 1799; from *Ber. Deut. Pharm. Ges.*, 16, 110—115).—Of the recently introduced apparatus for this purpose, the large Lohnstein saccharometer is recommended.

L. DE K.

New Apparatus for the Estimation of Sucrose in Beet. E. VIVIANI and D. GALEATI (*Chem. Centr.*, 1906, i, 1628; from *Bull. Assoc. Chim. Sucre Dist.*, 23, 1015—1016).—An automatic device for delivering a certain quantity of basic lead acetate solution which has to be added to the beet pulp.

L. DE K.

Estimation of Sucrose in Italian Beet. E. VIVIANI and D. GALEATI (*Chem. Centr.*, 1906, i, 1628; from *Bull. Assoc. Chim. Sucre Dist.*, 23, 1016—1020).—Pellet's cold-water extraction process is stated to be quite satisfactory.

L. DE K.

New Source of Error in the Estimation of Sugar in Beet. HENRI PELLET (*Chem. Centr.*, 1906, i, 1676; from *Bull. Assoc. Chim. Sucre Dist.*, 23, 1013—1014).—The substitution of alcohol for water has been recommended in the extraction of beet for analytical purposes. The author states that the extraction of the sugar by alcohol is somewhat incomplete, as cellular matter has the property of retaining sucrose. This source of error is absent when water is used for the extraction.

L. DE K.

Test for Sucrose in Milk-sugar. HENRY LEFFMANN (*Chem. Zeit.*, 1906, 30, 638).—The well-known test for sesamé oil by means of hydrochloric acid and sucrose may be used reversedly for the detection of sucrose in milk-sugar.

One c.c. of sesamé oil is mixed with 1 c.c. of strong hydrochloric acid and 0.5 gram of the suspected milk-sugar is added. In the presence of even 1 per cent. of sucrose, the liquid on being thoroughly shaken gives the characteristic colour within 30 minutes. L. DE K.

Estimation of Sugars and Starch in Chocolates. HENRI PELLET (*Ann. Chim. anal.*, 1906, 11, 207—210).—A criticism of the method proposed by Robin (this vol., ii, 499). No account is taken by Robin of the increase in volume caused by the soluble sugars or of any moisture in the sample. (If the amount of sugar were 5 grams, that would increase the volume of the liquid by 3.6 c.c.). The author objects to the use of basic lead acetate and prefers the normal salt. The inversion of the residual starch should be effected by heating on the water-bath with dilute sulphuric acid for 3 hours.

L. DE K.

Bleaching of Flour. ÉMILE FLEURENT (*Bull. Soc. chim.*, 1906, [iii], 35, 381—396).—The natural yellow tint of the better grades of flour is due to the presence of about 1 per cent. of a yellow oil, whilst the darker colour of the lower grades is due to the inclusion of ground bran. The coloration due to oil may be removed by the action of chlorine or nitrogen peroxide and the latter is the active agent in the flour-bleaching processes in actual use, devised by Andrews, by Alsop, and by Teisset. The nitrogen peroxide combines with the oil, forming a product which has a higher "acid number," a lower "iodine number," and absorbs less light than the natural oil. It is to the change in optical property of the oil that the apparent bleaching of the flour is due. In the case of low grade flour containing bran, no bleaching is effected by nitrogen peroxide because the reagent is used up in oxidising the cellulose of the bran and the contained oil is for the most part not acted on. No change in the composition of the flour, apart from the oil, is brought about by treatment with nitrogen peroxide.

Flours bleached by this reagent may be detected (1) by extracting the oil with benzene and comparing its colour with that of oil extracted by the same solvent from unbleached flour, or (2) by comparing the colour of the potassium soap yielded by oil from the suspected sample with the colour of the soap furnished by oil from unbleached flour. Full details of the methods of applying these tests are given in the original.

Bleached flour becomes rancid less rapidly than unbleached flour when kept, and the bleaching appears to have no deleterious action on the activity of the enzymes present.

T. A. H.

Action of Flour on Hydrogen Peroxide. W. BREMER (*Zeit. Nahr. Genussm.*, 1906, 11, 569—577).—Processes for ascertaining the quality of flour based upon the property bran has of evolving more oxygen from hydrogen peroxide than does flour, are shown to be untrustworthy. The quantity of oxygen evolved is not proportional to the weight of the portion of the sample employed for the experiment or to the dilution of the hydrogen peroxide. Experiments with bran itself show that its power of decomposing hydrogen peroxide is diminished considerably by previous heating and is inhibited by the presence of mercuric chloride and of hydrochloric acid. Both the insoluble residue and the soluble portion, obtained on extracting bran with water, decompose hydrogen peroxide; whether two separate substances having this property are present, or whether the one substance is soluble with difficulty, the author has not yet ascertained.

W. P. S.

Microscopical Examination of Flours and Detection of Rice in Wheat Flour. G. GASTINE (*Compt. rend.*, 1906, 142, [xxii], 1207—1210).—A very small quantity of the suspected flour is put on to an object glass and moistened with two drops of staining fluid. For this may be used a 0.05 per cent. alcoholic solution of various blue, green, brown, or orange coal-tar colours.

After drying at 28—30° the mass is exposed for a few minutes to a temperature of 110—130°, then moistened with a drop of cedar oil or

Canada balsam, and finally examined microscopically. Rice starch is particularly characterised by a rather large hilum, which is but rarely visible in wheat starch. Maize-flour behaves in this respect like rice.

L. DE K.

Detection of Formaldehyde. METH (*Chem. Zeit.*, 1906, 30, 666).—The reaction with phenylhydrazine hydrochloride, sodium nitroprusside, and sodium hydroxide which gives a blue coloration with formaldehyde is recommended in cases where there is a possibility of acraldehyde occurring.

L. DE K.

Action of Iodine on Acetoacetic Acid and Detection of this Acid in Urine. SAMUEL BONDI (*Chem. Centr.*, 1906, i, 707—708; from *Wien Klin. Wochschr.*, 19, 37—39).—If iodine solution is added to acetoacetic acid in presence of excess of barium carbonate, barium iodoacetoacetate is formed which gradually, especially on warming, yields barium carbonate and iodoacetone.

For the detection of acetoacetic acid in urine, iodine solution is added to 5 c.c. of warm urine until the liquid remains orange-red. On boiling, the characteristic pungent odour of iodoacetone will be noticed. If the amount is supposed to be very small, the boiling liquid should be poured on to a large watch-glass. The urine should be neutral or faintly acid; alkaline urine should, therefore, be slightly acidified with acetic acid. The test is not interfered with by acetone or β -hydroxybutyric acid.

L. DE K.

Composition of Milk. H. DROOP RICHMOND (*Analyst*, 1906, 31, 176—180).—The mean composition of the milk examined during the year 1905, as shown by the analyses of 14,828 samples, was practically the same as that found in 1904 (*Abstr.*, 1905, ii, 869), the average amount of fat differing only by 0.01 per cent. As usual, the lowest percentage of fat was found in the months of May and June, and the highest in the winter months.

A recently-introduced butter adulterant was analysed and found to consist of casein, 30.50 per cent.; water, 65.47 per cent.; sugar 2.24 per cent., and small quantities of ash, soluble proteids, and fat. A preservative, sold under the name of "acid potassium oxalate," consisted of potassium hydrogen fluoride, KHF_2 .

W. P. S.

Detection of Cocoanut Oil in Butter. ARTHUR W. THORP (*Analyst*, 1906, 31, 173—175).—The process described is a continuation of the Reichert-Wollny test. One hundred and ten c.c. of distillate are collected as usual, cooled, filtered, and titrated. If there is a considerable quantity of cocoanut oil in the sample, oily drops will appear on the surface of the distillate. After the addition of 110 c.c. of water to the flask, the distillation is continued and 110 c.c. of distillate are collected, passed through the filter previously used, and titrated. The condenser, measuring vessels, and filter are now washed with hot alcohol and the solution obtained, titrated. The second distillate in the case of pure butter requires from 2.9 to 4.0 c.c. of $N/10$ alkali for neutralisation and the alcoholic solution from 5.2 to 8.4 c.c. of $N/10$ alkali.

Cocoonut oil gives a second distillate which requires 4.0 c.c. of *N*/10 alkali, whilst the alcoholic solution of the insoluble volatile fatty acids needs 34.0 c.c. The results of analyses of mixtures containing varying proportions of butter and cocoonut oil are given, showing that the quantity of alkali required for the neutralisation of the alcoholic solution increases with the amount of cocoonut oil present in the sample.

W. P. S.

Karité Butter. FERDINAND JEAN (*Ann. Chim. anal.*, 1906, 11, 201—203).—Attention is called to the importation of large quantities of this fat which is obtained from the seeds of *Bassia butyracea* and is used chiefly in admixture with lard, margarine, cocoa fat and oils for the adulteration of butter. The analysis of butter is thus rendered still more complicated and uncertain.

A sample prepared by the author from the seeds showed: oleo-refractometer at 45°, +22°, melting point 30°, saponification number 175—176 KOH, Reichert M.W. number 2.6, *N*/10 alkali, soluble volatile acids (as butyric) 0.211, insoluble ditto 1.05, relation between the volatile insoluble and soluble acids $\times 100 = 497$.

An analysis of the butter as imported is given, also that of a butter adulterated with the same. An addition of Karité butter to ordinary butter lessens the index of the oleo-refractometer, lowers the saponification number, the Reichert number, and also the (Wijsman's) silver number, raises the Hehner number and the relation between the insoluble and soluble volatile acids (Muntz and Coudon's method).

L. DE K.

Detection of Foreign Oils in Nut Oil. PIERRE BALAVOINE (*Chem. Centr.*, 1906, 1, 1677; from *Schweiz. Woch. Chem. Pharm.*, 44, 224—226).—The author approves of the saponification process recommended by Bellier (*Abstr.*, 1905, ii, 292). Poppy oil may be detected in nut oil if present to the extent of at least 20 per cent.; olive, sesamé, cotton, and ground-nut oils give the reaction when they exist to the amount of 5—10 per cent.

L. DE K.

Assay of Bee's Wax. P. BOHRISCH and RUDOLF RICHTER (*Chem. Centr.*, 1906, 1, 1717; from *Pharm. Centr.-Halle.*, 47, 201—213, 227—233, 270—278, 299—304, 311—313).—A criticism of the various methods in use for the assay of bee's wax. The use of Zeiss's refractometer is recommended as a good test for the presence of paraffin, stearin, and carnauba wax. Undue importance should not be attached to the colour of the samples.

L. DE K.

New Tests for Cocaine. C. REICHARD (*Chem. Centr.*, 1906, i, 1764—1765; from *Pharm. Centr.-Halle.*, 47, 347—353. Compare *Abstr.*, 1904, ii, 374; 1905, ii, 127).—If cocaine hydrochloride is moistened with stannous chloride solution, then with excess of sodium hydroxide, evaporated to dryness and heated, the mass turns dark grey or black. Morphine behaves similarly, but if treated with sodium stannate, the alkaloids show a difference, for in such case cocaine is quite unaffected. If a mixture of cocaine with white precipitate is

moistened with a drop of aqueous sodium hydroxide, the mass turns yellow, but if morphine is present the mixture turns black. If a coarse mixture of cocaine hydrochloride and mercuric chloride is moistened with aqueous sodium hydroxide, black crystals are noticed in the yellow mass of mercuric oxide. If a mixture of cocaine hydrochloride and ammonium persulphate is gently warmed with aqueous sodium hydroxide, a somewhat violent reaction takes place, and a red or reddish-brown substance is formed.

When a solution of cocaine hydrochloride in a drop of sulphuric acid is heated, a blue zone is formed, and the mass gradually turns a black colour. When warmed with nitric acid, cocaine is converted into a colourless varnish, which, however, is not affected by alkaline stannous chloride. If hydrochloric acid is used instead, a bluish-black colour will be obtained. If a mixture of cocaine hydrochloride and sodium metasulphite is moistened with a few drops of water and nitric acid and evaporated to dryness, and if the residue is then heated with aqueous sodium hydroxide and mixed with ammonia, a blue or grey coloration is formed. If cocaine hydrochloride is heated with a drop of strong bismuth chloride and then mixed with excess of aqueous sodium hydroxide, a separation of white bismuth hydroxide takes place immediately, whilst in the case of morphine, the mass turns a dark reddish-brown.

L. DE K.

Use of Carbon Tetrachloride in Investigating the Colouring Matters Prohibited in Food by the Sanitary Law. ARNALDO PIUTTI and G. BENTIVOGLIO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1905, [iii], 11, 457—462).—The use of Martius-yellow, metanil-yellow, Victoria-yellow, or picric acid is prohibited in foods in Italy, whilst naphthol-S.-yellow is admissible. The existing methods of detection do not give good results when several of these colours are present together, but by the use of carbon tetrachloride they are readily detectable.

On treating an acetic acid solution of the colours with carbon tetrachloride, (1) Martius-yellow and Victoria-yellow pass into solution. These are dissolved in aqueous ammonia and one part of the liquid is treated with stannous chloride and ammonia, when a red precipitate indicates the presence of Martius-yellow; another part is treated with zinc and hydrochloric acid, a red solution then showing the presence of Victoria-yellow; (2) metanil-yellow, picric acid, and Naphthol-S.-yellow remain in the acetic acid solution, which is evaporated to dryness on a water-bath and the residue dissolved in water. To one part of this solution, hydrochloric acid is added, the presence of metanil-yellow (tropæolin G.) being indicated by a violet coloration; another part is mixed with ammonium hydrosulphide, the formation of a reddish-brown coloration showing the presence of picric acid; the existence in the liquid of naphthol-S.-yellow is demonstrated by reducing the third part, firstly with zinc and ammonia, then with zinc and hydrochloric acid, and treating (a) with potassium hydroxide, which yields a yellow coloration, and (b) with ferric chloride solution, which gives an orange coloration.

T. H. P.

Estimation of Proteids in Milk. AUGUSTE TRILLAT and SAUTON (*Compt. rend.*, 1906, 142, 794—796).—Five c.c. of the sample are diluted with 25 c.c. of water and boiled for five minutes, when five drops of commercial formalin are added. After boiling for a few minutes longer, the liquid is allowed to cool for five minutes and 5 c.c. of 1 per cent. acetic acid are added. The precipitate is then washed and freed from fat by treatment with acetone in an extractor and finally dried at 75—80° and weighed. The method is applicable to milk of different animals and also to samples preserved with potassium dichromate. Experiments are communicated showing that the action of formaldehyde does not affect the weight and composition of the proteids.

L. DE K.

The Guaiacum Test for Blood. C. E. CARLSON (*Zeit. physiol. Chem.*, 1906, 48, 69—79).—The guaiacum test is improved by the addition of hydrogen peroxide to the oil of turpentine containing ozone. This oil when old and preserved from air and light contains no ozone, and is of no use in the test. It contains no hydrogen peroxide. Its use in the test depends on the formation of molecularly united hydroxyl groups. The blue coloration of guaiacum tincture by blood in the presence of turpentine or hydrogen peroxide depends on the presence in the blood of an organic compound, which takes up hydroxyl to form a labile union; this gives up the hydroxyl to the guaiacum almost instantaneously, and the result is the blue colour.

W. D. H.

Diastatic Catalysis of Hydrogen Peroxide applied to Malt Analysis. HENRI VAN LAER (*J. Inst. Brewing*, 1906, 12, 313—338).—The determination of the catalytic activity of a barley or malt must be made with hydrogen peroxide solution containing no sulphuric or hydrochloric acid such as Merck's 30 per cent. perhydrol. A solution containing 1.7 grams of the peroxide per 100 c.c. is of convenient strength, and sufficient for the experiments of the day should be kept in a paraffined flask so as to avoid the catalysing action of the glass; the concentration of this solution is insufficient to destroy the catalysing matters introduced either by the air or by the distilled water used. Twenty-five c.c. of this solution are taken and 6 grams of the finely-powdered barley or malt. These are placed in an Erlenmeyer flask so as not to mix, the flask having been connected previously with a Hempel burette containing water which has been adjusted to the zero mark. A tapped stopper is then fitted to the flask, the tap being afterwards closed. The malt and peroxide solution are now mixed by shaking the flask for exactly ten seconds, and the volume of gas evolved read every five minutes.

The volumes of oxygen evolved during successive periods of five minutes decrease much more rapidly in the case of malt than in that of barley. So that malts the catalytic activities of which appear to be greater than that of the corresponding barleys when the reading is made at the end of five minutes show lower catalytic activities than the barleys if the volumes of gas are compared at a later phase of the experiment. The catalase of malt is therefore more quickly destroyed by the action of hydrogen peroxide than that of barley.

The catalytic activity increases during the steeping of the barley and germination, and decreases during kilning; it undergoes during kilning two sudden falls: one when the green malt containing 40—45 per cent. of moisture is in twenty-four hours transformed into hand-dry malt with only 6—8 per cent. of moisture, and the other at the end of the kilning operation, when the temperature is raised to 105°; the rapid passage through intermediate temperatures diminishes but slightly the catalytic activity. Diastatic power exhibits similar behaviour. Considering the sensitiveness of catalase to heat in the presence of moisture, it is certain that if all secretion of catalase ceased at the commencement of kilning, the fall in the catalytic activity after twenty-four hours on the kiln would be more accentuated than is indicated by the numbers obtained.

Roughly, a high catalytic activity indicates a high diastatic activity, and a low catalytic activity points to a low diastatic activity, although it is not possible exactly to measure one by the other.

When the catalytic activity of a malt and the specific rotatory power are reconcilable, the probable attenuation on fermentation indicated by one figure is confirmed by the other. When the figures are contradictory, it is best to trust to the catalytic activity, except in those cases where the specific rotatory power is too high compared with the catalytic activity; in the last event, attention will be called to the inadequate friability of the malt or some other circumstances capable of raising the specific rotatory power.

T. H. P.

Estimation of Organic Phosphorus Compounds in Flour and Pastry. CH. ARRAGON (*Zeit. Nahr. Genussm.*, 1906, 11, 520—521).—Fifty grams of the finely-powdered sample are boiled with 150 c.c. of alcohol for one hour. A reflux apparatus is used to prevent excessive evaporation of the alcohol, and the flask with its contents is weighed before and after the boiling; any loss of alcohol is made up by the addition of a further quantity. One hundred c.c. are then filtered off, evaporated after the addition of 2 grams of potassium nitrate and 3 grams of sodium carbonate, and the residue ignited. The ash is next dissolved in nitric acid, the phosphoric acid precipitated by means of molybdic acid solution, and the precipitate obtained converted into ammonium magnesium phosphate in the usual manner.

W. P. S.

Bacteriological Testing of Disinfectants. THOMAS H. LLOYD (*J. Soc. Chem. Ind.*, 1906, 25, 405—408).—In order to obtain greater concordance in the results yielded by the Rideal-Walker method (*J. Sanit. Inst.*, 1903), it is recommended that distilled water only should be used for dilution, and agar cultures abandoned in favour of broth, the latter being filtered through ordinary paper to remove clumps. The phenol used as the standard must be titrated with bromine in order to obtain its exact strength, as the crystallised "carbolic acid" on the market contains varying amounts of water. The composition of the broth and its reaction is also of importance.

W. P. S.

General and Physical Chemistry.

New Burner for Spectroscopic Use. E. H. RIESENFELD and H. E. WOHLERS (*Chem. Zeit.*, 1906, 30, 704—705).—By electrolysing a small quantity of a salt solution by means of wire electrodes at the base of a Bunsen burner, the bubbles of gas resulting from the electrolysis carry with them small quantities of the liquid and are drawn together with the air into the flame, which is thereby coloured. When using copper or thallium salts, in which the metal is likely to be deposited on one of the electrodes, the current should be reversed at intervals of a minute by means of a commutator introduced into the circuit. P. H.

Radioactivity of the Soil and Mineral Waters of Slănic (Roumania). ÉMILE SEVERIN and DRAGOMIR HURMUZESCU (*Ann. Sci. Univ. Jassy*, 1906, 4, 85—86).—As it has been shown by various observers in recent years that many mineral waters are radioactive, the authors have examined from this point of view the waters from the district indicated above. It was found that deposits from the waters have distinct radioactive properties, and preliminary experiments by the electroscope method indicate that the same is true of the gases obtained from the waters. G. S.

Measurement of Radium in Minerals by the γ -Radiation. A. S. EVE (*Amer. J. Sci.*, 1906, [iv], 22, 4—7. Compare this vol., ii, 259).—On account of the ready absorption of the γ -rays from uranium and actinium as compared with those of radium, thorium, and radiothorium, the radiation from the former elements can be cut off and the amount of radium or thorium present in any ore or solution can then be determined by comparison with a standard quantity of radium or thorium. If the ore contains a mixture of these two elements, the method can only be applied to obtain their joint amount.

Radium E, which is probably present in equilibrium amount in uraninite, emits either no γ -rays or rays which are readily absorbed. In connection with comparative measurements, it has been found that standard solutions of radium bromide decrease in strength unless acid is present; this is due to deposition on the sides of the containing vessel. Such standard solutions should be controlled by comparison with a standard sealed tube containing solid radium bromide.

H. M. D.

Relative Proportion of Radium and Uranium in Radioactive Minerals. ERNEST RUTHERFORD and BERTRAM B. BOLTWOOD (*Amer. J. Sci.*, 1906, [iv], 22, 1—3. Compare Abstr., 1905, ii, 568, and preceding abstract).—The neutral standard solution of radium bromide previously used in measuring the amount of radium present per gram of uranium in a natural mineral has been found to be incorrect in consequence of the gradual deposition of some of the dissolved substance from the

solution. A new standard solution, acidified with hydrochloric acid and compared with a known quantity of solid radium bromide, has now been used for the determination. With this, the quantity of radium associated with one gram of uranium is found to be 3.8×10^{-7} gram. This quantity is about one-half of that given by the first measurement.

H. M. D.

Periods of Transformation of Radium *A*, *B*, and *C*. HOWARD L. BRONSON (*Phil. Mag.*, 1906, [vi], 12, 73—82. Compare Abstr., 1905, ii, 567; von Lerch, this vol., ii, 514).—The experimental decay curves for the active deposit from radium agree with the theoretical decay curves, calculated on the assumptions that the three products *A*, *B*, and *C* are successive, and that their periods (that is, times necessary for decay of activity to half value) are respectively three, twenty-six, and nineteen minutes. As observed by Schmidt, radium *B* emits β -rays of less penetrating power than those from radium *C*; on this account the β -ray decay curves are unsuitable for purposes of analysis.

J. C. P.

Quantitative Separation of Radiothorium from the Mud of Echaillon and Salins Moutier. OTTORINO ANGELUCCI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 497—500. Compare Blanc, this vol., ii, 323).—Although radiothorium is precipitated quantitatively by means of ammonia, it is also precipitated quantitatively along with the sulphate or carbonate of calcium, and it also forms an insoluble oxalate. It therefore belongs more probably to the ammonium carbonate group than to the ammonia group.

On treating the hydrochloric acid extract of the mud from Echaillon and Salins Moutier with ammonia, some of the active hydroxide remains in solution. If the calcium is precipitated from the hydrochloric acid solution as sulphate, almost the whole of the active substance is carried down and can be washed out with water; this does not, however, effect a separation from iron salts. This can be effected by making use of the solubility of ferric chloride and insolubility of calcium sulphate in alcohol, a precipitate being thus obtained containing only calcium sulphate and radiothorium. On dissolving this precipitate in hydrochloric acid and adding ammonia to the solution, the whole of the active substance is precipitated.

The sulphates of calcium, strontium, and barium dissolve in a solution of thorium chloride or nitrate, forming double salts.

T. H. P.

Some Properties of the α -Rays of Radiothorium. II. OSKAR HAHN (*Phil. Mag.*, 1906, [vi], 12, 82—93. Compare this vol., ii, 416).—The present paper deals with the ionisation ranges of radiothorium, thorium *X*, and the emanation: the values of these are found to be 3.9 cm., 5.7 cm., and 5.5 cm. respectively. The range of the α -rays from thorium *B* is probably 5.0 cm., and not 4.7 cm., the value given in the previous paper. If it is assumed that the α -particles from thorium and radium are the same in all respects, then it follows that the α -particles from the thorium products are, on

the average, projected with greater velocity than the α -particles from the radium products. Further, the velocity of the α -particles from radium *C* and thorium *C* is much greater than that of the α -particles from the other products.

J. C. P.

Absorption of α -Rays from Polonium. MAX LEVIN (*Amer. J. Sci.*, 1906, [iv], 22, 8—12).—The range of ionisation of the α -particles from polonium has been determined by experiments with a bismuth rod coated with polonium. Using a zinc sulphide screen, the distance at which the scintillations just disappeared in air was found to be 3.78 cm. By the electrical method, the value obtained was 3.86 cm., and by varying the distance between the source and the measuring instrument ionisation curves were obtained similar to those previously found for the α -rays from radium and radium *C*. Interposition of aluminium foil does not alter the general form of the curve, which is simply displaced by an amount corresponding with the stopping power of the aluminium sheet. The amount of the maximum ionisation is not affected by the absorption of the α -rays in the foil, indicating that the α -rays are not absorbed according to an exponential law, but that the whole of the α -particles pass through it, the velocity in every case being diminished by a definite amount. The α -particles from polonium are therefore homogeneous, and are projected with the same initial velocity. The range of the particles is slightly greater than that of the radium particles (3.50 cm.), but much less than that of the radium *C* particles (7.06 cm.).

H. M. D.

Chemical and Physical Behaviour of the Nickel Oxide Electrode in the Jungner-Edison Accumulator. JULIAN ZEDNER (*Zeit. Elektrochem.*, 1906, 12, 463—473. Compare this vol., ii, 65).—By keeping nickelic hydroxide at about 8° over sulphuric acid of various strengths it was found that when the partial pressure of the aqueous vapour over the sulphuric acid was less than 3 mm. the hydroxide has the composition $\text{Ni}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, whilst between 3 and 7 mm. the composition is $\text{Ni}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$.

The *E.M.F.* of cells made up of a nickelic hydroxide electrode and a hydrogen electrode in solutions of potassium hydroxide was measured. The *E.M.F.* diminishes as the concentration of the solution increases, which indicates that water takes part in the change which occurs. An application of the laws of concentration cells leads to the conclusion that the change is $\text{Ni}(\text{OH})_3 + 2\text{H}_2\text{O} \rightleftharpoons \text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O} + \text{OH}'$ in solutions containing more than twenty-four per cent. of potassium hydroxide. The temperature-coefficient of the *E.M.F.* of the cell $\text{Ni}(\text{OH})_3 \mid \text{twenty-five per cent. KOH} \mid \text{H}_2$ is, between 10° and 65°, -0.0007 volt per degree. Since the reaction $\text{Ni}(\text{OH})_3 + \text{H} = \text{Ni}(\text{OH})_2 + \text{H}_2\text{O}$ develops 34,800 cals., it follows by applying Helmholtz's equation that the *E.M.F.* of the cell at 10° should be 1.308 volts, the value found being 1.305 volts.

When a nickelic hydroxide electrode is discharged, its *E.M.F.* first falls slowly; this is shown to be due to the increasing concentration of the potassium hydroxide solution in contact with it, owing partly to the absorption of water by the chemical reaction and partly to the

electrolytic migration of potassium ions towards the electrode. When the readily available nickelic hydroxide is reduced, a rapid fall of the *E.M.F.* occurs to a second stationary value; this is shown to be due to occluded oxygen, which may be removed by placing the electrode in a vacuum or by heating the solution in contact with it. The occlusion appears to be due mainly to the graphite which is usually mixed with the nickelic hydroxide. A discharged electrode recovers its original *E.M.F.* after a time owing to the diffusion of water into its pores.

T. E.

Validity of Faraday's Law for Metals yielding Ions of Different Valency. RICHARD ABEGG and IWAN SHUKOFF (*Zeit. Elektrochem.*, 1906, 12, 457—459).—If a metal which is capable of forming ions of different valency is in equilibrium with a solution containing both kinds of ions, then when an electric current is passed the two kinds of ions should separate out in the proportions in which they are present in the solution. In a solution of mercurous nitrate, in presence of mercury, 99.6 per cent. of the mercury exists in the mercurous condition as Hg_2^{++} ions and 0.4 per cent. as Hg^{++} ions. Experiments in which both the anode and cathode were weighed gave a loss or gain of weight of 99.3 to 99.7 per cent. of that which would have been observed if the mercury had been dissolved or deposited exclusively in the mercurous form.

The case of complex mercuric ions is discussed, and the conclusion is reached that both at the anode and cathode the solution would behave as if it contained mercuric ions alone, owing to the fact that there is no reservoir from which mercurous ions can be supplied as they are removed by the electrolysis. An experiment showed that mercury is dissolved by or deposited from a solution of potassium mercuric iodide as mercuric mercury, whereas the same solution in presence of solid mercurous iodide deposits or dissolves the metal as mercurous mercury.

T. E.

Types of Diaphragms most used in Electrolysis and Formulæ proposed for Calculating the Yield. UGO LOMBARDI (*Gazzetta*, 1906, 36, i, 378—387).—The author shows that none of the formulæ known up to the present can be used in practice for calculating the yield in the electrolysis of the alkali chlorides. It is difficult to find one which can be so used, since, even if empirical, it has to take into account too many factors, some of which cannot be determined in practice; this is the case, for example, with the diffusion of the hydroxide through the diaphragm, which depends on the nature, thickness, and area of the diaphragm, and also with the electrical endosmose.

As regards the behaviour of the different types of diaphragm in the electrolysis of the alkali chlorides and the criteria for determining the choice of one rather than the other, nothing absolute can be asserted. In normal conditions, the fall of potential produced by a porous septum varies from a minimum of 0.1 to a maximum of 0.2 volt.

Another factor varying greatly, even with diaphragms of the same

type, is the permeability, which depends on the structure of the material. Thus, the porous septa of Pukall and Villeroy have numerous, very small pores, which, on the one hand, increase the resistance, and, on the other, render the diffusion slower and the permeability less. Septa of asbestos are more porous and far more permeable, since their structure is that of a felt in which the fibres are interlaced; electrically they are less resistant and the diffusion through them proceeds more easily, so that, in the electrolysis of the alkali chlorides, the concentration of the hydroxide, which for economy's sake should not exceed a certain value, is less than with other porous septa. Diaphragms of cement are more resistant and less porous than the others; their pores are irregular and too large, so that the diffusion is greater than with other diaphragms, but they are more economical than the latter.

The essential differences between the various types of diaphragms are not marked, each having certain advantages and disadvantages. The choice in any particular case depends mainly on the conditions and on the chemical nature of the substance to be electrolysed.

T. H. P.

Thermodynamics of Heterogeneous Hydrolytic Equilibrium.

FRIEDRICH DOLEZALEK and KARL FINCKH (*Zeit. anorg. Chem.*, 1906, 50, 82—100).—The heterogeneous hydrolytic equilibrium for a monovalent metal is represented by the equation $MR + H_2O \rightleftharpoons M\cdot OH + HR$, where M denotes the metal and R the acid residue. In the case of multivalent metals, several molecules of water take part in the action. When the oxide is formed instead of the hydroxide, the amount of water entering into reaction will be correspondingly smaller.

The case here considered is that in which the base and acid are only slightly soluble; their concentrations in the liquid phase may therefore be regarded as constant and the equilibrium is then determined solely by the concentration of the acid: in other words, for a given temperature there is a definite concentration of acid in equilibrium with the other phases; this may be called the limiting concentration. For the case in question, an expression has been obtained for the maximum work of hydrolysis under certain definite conditions by means of a cyclic process. Further, an expression for the displacement of the limiting concentration with temperature has been obtained by a simple application of the second law of thermodynamics, and it is shown that increase of temperature invariably displaces the equilibrium in the direction of greater acid concentration. The case in which there is intermediate formation of basic salts is also taken into account and it is shown that the number of solid basic salts capable of existing rapidly decreases with rise of temperature.

These theoretical deductions have been tested by application to the hydrolysis of lead disulphate, $Pb(SO_4)_2$, which fulfils satisfactorily the above conditions. Measurements of electromotive force show in the first place that the hydrolysis takes place in the following two stages: (1) $Pb(SO_4)_2 + 2H_2O = PbOSO_4\cdot H_2O + H_2SO_4$; (2) $PbOSO_4\cdot H_2O = PbO_2 + H_2SO_4$, the oxysulphate and peroxide being in equilibrium with different concentrations of acid. When this is taken into

account, the value for the maximum work of hydrolysis, obtained directly from the measurement of *E.M.F.*, is in excellent agreement with that calculated by means of the expression referred to in the last paragraph. Further, the energy given out during hydrolysis has been determined by calorimetric measurements, and by means of this value the displacement of the limiting acid concentration with temperature has been calculated; the coefficient is in good agreement with that obtained directly.

G. S.

Electrical Resistance Furnace for the Measurement of High Temperatures with the Optical Pyrometer. ALEXANDER LAMPEN (*J. Amer. Chem. Soc.*, 1906, **28**, 846—853).—The furnace described has been devised for ascertaining the temperatures at which certain physical and chemical changes take place. The walls are made of fire-brick and lined with a mixture of fire-clay and siloxicon. The terminals are Acheson graphite electrodes, of which the parts outside the furnace are coated with asbestos. The most noteworthy feature of the apparatus is a horizontal graphite tube of 30 mm. diameter which is placed across the middle of the furnace through holes in the walls. The substance to be heated is placed in a small graphite capsule and inserted in the end of a second tube, which is of such a diameter as to slide easily into the first tube. On passing the current through the furnace, the temperature is highest in the middle and decreases towards the ends. By regulating the current and moving the sliding tube in a suitable manner, the required temperature may be easily reached and maintained, the readings being taken through the end of the tube by sighting with the pyrometer on the capsule. When it is desired to take out the substance, the sliding tube is withdrawn and the capsule removed with a carbon rod. In this way, by heating the substance repeatedly to higher temperatures by known intervals, it is possible to ascertain the approximate temperature at which a particular change takes place. For details of the apparatus and method of working, reference should be made to the description and diagrams in the original.

By the use of this furnace it has been found that the reaction between carbon and silica begins at 1615°, and that the formation of crystallised silicon carbide or carborundum commences at 1900—2000°, and its decomposition into silicon and graphite at 2200—2240°. Similarly, it is shown that when a mixture of calcium oxide and carbon is heated, calcium carbide begins to be formed at about 1725°. Melting points are recorded of certain refractory materials such as fire-clay, fire-brick, and porcelain. Pure quartz becomes rounded at the edges at 1650°, and fuses at 1700°. Magnesia, previously fused in the electric arc, melts at 2000°.

E. G.

Thermal Constants of Acetylene. WILLIAM G. MIXTER (*Amer. J. Sci.*, 1906, [iv], **22**, 13—18).—The heat developed in the dissociation and combustion of acetylene has been measured. The results are compared with the author's data for the heats of combustion of hydrogen and acetylene-carbon:

Heat of combustion of hydrogen	68440 cal.
„ „ „ acetylene-carbon	189456
„ dissociation of acetylene	53879
		<hr/>
		311775
Heat of combustion of acetylene	312677
		<hr/>
	Difference	902

No evidence of the production of radioactive gases in the explosive dissociation of acetylene was obtained. H. M. D.

Magnitude of the Liquid Molecules of Certain Organic Compounds. GIACOMO CARRARA and G. FERRARI (*Gazzetta*, 1906, **36**, i, 419—429).—The following association factors have been determined :

Methyl alcohol, 3.33 at 16—46°, 3.26 at 46—78°, and 2.89 at 78—132°. *n*-Butyl alcohol, 2.978 at 22—30°, 2.728 at 30—40°, 1.99 at 40—50°, and 1.61 at 50—60°. *sec*-Butyl alcohol, 2.191 at 24—34°, 1.589 at 34—41°, 1.306 at 41—52°, 1.024 at 52—62°, 0.975 at 62—70°, and 0.915 at 70—80°. *tert*-Butyl alcohol, 1.934 at 26—36°, 1.515 at 36—40°, 1.268 at 40—45°, 1.073 at 45—55°, 1.015 at 55—63°, and 0.978 at 63—70°. Hexyl alcohol, 2.084 at 25—35°, 1.561 at 35—40°, 1.041 at 40—45°, 0.959 at 45—54°, 0.892 at 54—62°, 0.891 at 62—72°, 0.884 at 72—80°, and 0.817 at 80—86°. Heptyl alcohol, 1.588 at 22—32°, 1.396 at 32—45°, 1.391 at 45—55°, 1.381 at 55—68°, 1.249 at 68—73°, 1.087 at 73—80°, and 0.953 at 80—85°. *n*-Octyl alcohol, 1.051 at 21—35°, 1.001 at 35—45°, 0.909 at 45—56°, 0.849 at 56—62°, 0.841 at 62—67°, 0.805 at 67—72°, and 0.719 at 72—76°. Acetaldehyde, 1.46 at 7—11°, 1.06 at 11—18°, and 0.88 at 18—21°. Paraldehyde, 0.91 at 20—30° and 30—39°, 0.90 at 39—50°, 0.87 at 50—59°, and 0.85 at 59—68°. Nitromethane, 0.935 at 20—31°, 0.905 at 31—40°, 0.853 at 40—47°, 0.846 at 47—54°, and 0.809 at 54—59°. Thiophen, 1.141 at 21—35°, 1.017 at 35—46°, 0.995 at 46—54°, 0.935 at 54—61°, 0.914 at 61—67°, 0.849 at 67—74°, and 0.805 at 74—85°. Ethyl sulphide, 1.034 at 16—31°, 0.975 at 31—40°, 0.960 at 40—52°, 0.903 at 52—62°, 0.896 at 62—75°, 0.886 at 75—79°, and 0.824 at 79—84°.

Thus, with the alcohols, the degree of association in general decreases as the number of carbon atoms increases, and the most highly associated of the butyl alcohols is the normal compound. There does not appear to be any relation between the association and the chemical constitution of the various compounds. The association has no influence on the dissociating properties of the solvents. T. H. P.

Determination of the Osmotic Pressures of Solutions by the Measurement of their Vapour Pressures. EARL OF BERKELEY and E. G. J. HARTLEY (*Proc. Roy. Soc.*, 1906, **A**, **77**, 156—169. Compare *Proc. Roy. Soc.*, 1903, **73**, 436).—In determining the relative vapour pressures of solvent and solution, the authors adopted the dynamical method due to Ostwald and Walker. The current of air, however,

instead of bubbling through the solvent and solution, was allowed to pass over their surfaces in specially constructed apparatus, each separate vessel in which consisted of four glass tubes sealed together by inverted U tubes. Each vessel was filled to the extent of about one-third with the required liquid, and was so fitted up that it could be oscillated, and its two ends raised and lowered alternately. The consequent flow of the liquid from end to end kept the solution stirred and periodically wetted the branches through which the current of air passed. When the current of air was slow (about two bubbles a second, as indicated in a bottle attached to the apparatus), saturation was practically complete in one such vessel. From the observed relative vapour pressure of solvent and solution, the osmotic pressure P of the latter was calculated by the formula $P = As/\sigma \log_e p/p_1$, where p is the vapour pressure of the water, p_1 the vapour pressure of the solution, s the density of water at the temperature of the experiment, and σ the vapour density of water vapour under the standard atmosphere A . The osmotic pressures calculated by the foregoing formula from the vapour pressures observed for some sucrose solutions agreed to within 5 per cent. with the osmotic pressures observed directly.

It should be noted that the authors' formula differs from the one given by Arrhenius: $P = A\rho/\sigma \log_e p/p_1$ in that they put s , the density of the solvent, instead of ρ , the density of the solution. This is done in order to give the osmotic pressure at the *top* of the column of solution (compare Spens, this vol., ii, 273). The paper contains a theoretical investigation of the question which leads to the required relation.

J. C. P.

Osmotic Pressure and Depression of the Freezing Point of Solutions of Dextrose. I. HARMON N. MORSE, JOSEPH C. W. FRAZER, and B. S. HOPKINS (*Amer. Chem. J.*, 1906, **36**, 1—39. Compare Abstr., 1905, ii, 575).—A detailed account is given of the means employed in the measurement of osmotic pressures to ensure accuracy by reducing the so-called "thermometer effects" to a minimum. The apparatus used for this purpose consists essentially of (1) a large bath containing more than 300 litres of water kept in constant motion; (2) an enclosure above the bath, the air in which is maintained in constant circulation through pipes immersed in the water beneath, and (3) various automatically regulated electric and gas stoves, which serve to maintain a fairly uniform temperature outside the bath.

A full description is given of the manner in which the difficulty connected with the form of the closed end of the manometer has been overcome, and also of an improvement which has been effected in the form of the open end of the manometer. An account is also given of corrections which are applied to the manometer readings and of an improvement which has been made in the cathetometer adjustment.

The closeness of texture which is indispensable in a good cell has rendered necessary a change in the method of expelling air from the walls, and instead of using potassium sulphate (Morse and Horn, Abstr., 1901, ii, 543) for the purpose, lithium sulphate is now employed. The results of a series of experiments with different salts have shown that the quantities of water carried through the porous

wall under identical conditions are inversely proportional to the relative velocities of the various cations divided by their respective valencies.

A number of observations are made with reference to the deposition and resistance of membranes and the prevention of leakage by the membranes.

In carrying out measurements of the osmotic pressure of dextrose solutions, the cells became affected by a growth of *Penicillium*. As the result of experiments it was found that the presence of the fungus could be prevented by means of thymol, even when used in quantities so minute that the pressures of the solutions were not appreciably affected by it. It was also found that thymol had no deleterious effect on the membranes.

The paper is illustrated with diagrams.

E. G.

Redetermination of the Osmotic Pressure and Depression of the Freezing Point of Sucrose Solutions. HARMON N. MORSE, JOSEPH C. W. FRAZER, E. J. HOFFMAN, and W. L. KENNON (*Amer. Chem. J.*, 1906, **36**, 39—93. Compare Abstr., 1905, ii, 575, and preceding abstract).—In carrying out the measurements of osmotic pressure, special efforts were made to reduce, as far as possible, the sources of error which were pointed out in the earlier paper. The conditions under which the experiments were conducted are described in detail, and the various measurements are tabulated and summarised.

The results confirm the conclusion which was deduced from the previous experiments, namely, that sucrose in aqueous solution exerts an osmotic pressure equal to that which it would exert if it were in the gaseous state at the same temperature and the volume of the gas were reduced to that of the solvent in the pure state. It is, however, at present uncertain whether the standard for the volume of the solvent in the pure state is its volume at maximum density or at the prevailing temperature.

The work on the freezing points and densities of sucrose solutions has shown that all concentrations conform to the following general rule. If Δ_1 represents the calculated depression of the freezing point, Δ its observed value, D the density of the solution at the temperature of freezing, and N its weight-normal concentration, then $\Delta_1 = 1.85 ND = \Delta$. This rule is not applicable to dextrose solutions.

The abnormally large depression of the freezing points of certain concentrated solutions is usually ascribed to the combination of a portion of the solvent with the dissolved substance. This explanation accounts satisfactorily for the peculiarities of the freezing point of sucrose solutions, but is not easily reconciled with the fact that there are no corresponding irregularities in the osmotic pressure, the pressure being always proportional to the concentration. It is suggested, however, that at the comparatively high temperatures at which the measurements were made the whole of the water acts as a true solvent, whilst at lower temperatures a portion of it unites with the sucrose, thus causing a concentration of the solution and, in consequence, an abnormal depression of the freezing point. In order to

decide this point, it is intended to determine the osmotic pressures of sucrose solutions at low temperatures. E. G.

Equilibria between Potassium Chromate and Barium Sulphate and Carbonate. MAX SCHOLTZ and RICHARD ABEGG (*Zeit. Elektrochem.*, 1906, 12, 425—428).—Equilibrium between barium sulphate and potassium chromate in aqueous solution is established very slowly; it is reached more rapidly when a solution of potassium sulphate acts on barium chromate. The experiments were made at 100°. The ratio between the quantities of potassium chromate and sulphate in solution when equilibrium is reached depends on the relative quantities of the solid barium salts, from which it appears that the precipitate consists of a solid solution. The relation $[K_2CrO_4]/[K_2SO_4] = 1.3[BaCrO_4]/[BaSO_4]$ appears to hold; the bracketed formulæ stand for the numbers of molecules. In the equilibrium between potassium chromate and barium carbonate, the ratio of the concentrations of potassium carbonate and chromate also varies in the same way as the ratio between the numbers of molecules of barium carbonate and chromate in the precipitate, but the two ratios are not proportional. There is, however, always relatively less chromate in the solution than in the precipitate. Barium chromate and sulphate are about equally soluble, and both are much less soluble than the carbonate. T. E.

Chemical Kinetics in Concentrated Sulphuric Acid. The Decomposition of Oxalic Acid. GEORG BREDIG and DAVID M. LICHTY (*Zeit. Elektrochem.*, 1906, 12, 459—463).—The rate of decomposition of oxalic acid dissolved in concentrated sulphuric acid agrees with the equation for the unimolecular reaction when the sulphuric acid contains more than 0.6 per cent. of water, the initial concentration of the oxalic acid being $N/40$. When the sulphuric acid is nearly pure, the rate of reaction is very much affected by small quantities of water, the addition of 0.1 per cent. of water being sufficient to increase the time required to reach a given stage in the change from one hour to seventeen hours. Between 0.15 and 3 per cent. of water the rate of decomposition is nearly inversely proportional to the square of the quantity of water added. Curves and tables are given representing the rate of change in sulphuric acid between 100 and 80 per cent., and at temperatures between 25° and 98°. T. E.

Chemical Kinetics. I. Hydrolysis of Ethyl Citrate. ALDO MIELI (*Gazzetta*, 1906, 36, i, 490—497).—In alcoholic solution, ethyl citrate is not hydrolysed by water, in which it is insoluble.

Hydrolysis of the ester by sodium hydroxide is very rapid, even at 0°, so that the time occupied in adding a quantity of hydrochloric acid equivalent to the amount of sodium hydroxide employed for the hydrolysis is relatively great compared with the total time of the reaction.

The values obtained for K_1 , K_2 , K_3 , or K_4 , assuming the reaction to be of the first, second, third, or fourth order, are not constant, and do

not oscillate about a mean value. The reaction calculated according to the integral method approximates to one of the first order, although the velocity of reaction is in no way independent of the concentration.

The author regards the reaction as taking place in more than one stage (compare Knoblauch, Abstr., 1898, ii, 423). T. H. P.

Affinity Constants of some Hydrolytic Products from Albumin. ARISTIDES KANITZ (*Zeit. physiol. Chem.*, 1906, 47, 476—495. Compare Winkelblech, Abstr., 1901, ii, 370; J. Walker, 1904, ii, 309; Lundén, this vol., ii, 265).—The dissociation constant K_x has been calculated by means of the equation $(1-x)v/x^2 = K_x/K_w$, where x is the degree of hydrolysis of a salt with a strong acid or a strong alkali, v is the dilution, and K_w is the ionisation product of water.

The dissociation constants for histidine at 25° are: first basic dissociation constant = 5.7×10^{-9} , and acid dissociation constant 2.2×10^{-9} .

The second basic dissociation constant has been calculated by means of a similar formula, in which v denotes the number of litres containing a gram-molecule of histidine dichloride, and x the amount hydrolysed to histidine hydrochloride and free hydrochloric acid. The value obtained was 5.0×10^{-13} .

The values for arginine and lysine are:

	Arginine.	Lysine.
First basic dissociation constant	$< 1.0 \times 10^{-7}$	$< 1.0 \times 10^{-7}$
Second „ „ „	2.2×10^{-12}	1.1×10^{-12}
Acid „ „ „	$> 1.11 \times 10^{-14}$	about $1-2 \times 10^{-12}$.

A comparison of the constants for lysine and leucine shows that the introduction of a second amino-group has increased the basic dissociation constant of leucine some 5×10^{-4} times, whereas the acid dissociation constant has been diminished some ten times only. J. J. S.

Molecular Constitution of Aqueous Solutions. WILLIAM SUTHERLAND (*Phil. Mag.*, 1906, [vi], 12, 1—20. Compare Abstr., 1901, ii, 92; 1902, ii, 300).—The author's theory of the molecular constitution of water when applied to the density, specific heat, and surface tension of aqueous solutions leads to the following conclusions: The contraction observed when electrolytes dissolve in water is due to their changing some of the trihydrol into dihydrol. The number of gram-molecules of $(H_2O)_3$ changed into $(H_2O)_2$ by a gram-equivalent of solute is the algebraic sum of two terms, one due to the positive ion and one to the negative ion. A positive ion changes $(H_2O)_3$ into $(H_2O)_2$, and a negative ion changes $(H_2O)_2$ into $(H_2O)_3$: a conclusion which is regarded as supplying a strong confirmation of the ionic dissociation theory.

The theory of the electric action of ions on $(H_2O)_3$ and $(H_2O)_2$ tends to confirm the existence in water of what has been called a stion (see Abstr., 1902, ii, 300); it is probable that the stion is an intermediate product in the ceaseless making and unmaking of $(H_2O)_3$ in water, and plays an important part in ionisation.

Consideration of the special properties of the H^+ and OH^- ions shows

that the exceptionally large ionic velocities usually assigned to these are not their true velocities, and that both these ions cause H_2O to dissociate into H' and OH' .

The author finds that the ionic velocity hitherto assigned to H' is the sum of 2.92 times the true velocity of H' and 1.92 times that of OH' . Similarly, the velocity hitherto assigned to OH' is the sum of 1.86 times the true velocity of OH' and 0.86 times that of H' .

The departure of the specific heats of solutions from the simple law of mixtures is traced to the change of $(\text{H}_2\text{O})_3$ into $(\text{H}_2\text{O})_2$ by the solute. In regard to the surface tension of solutions, the failure of the normal law for mixtures is traced to the same change. J. C. P.

Determination of the Solubility of Salt Mixtures at Temperatures considerably above the Boiling Points of their Saturated Solutions. HERMANN THIELE and ROBERT CALBERLA (*Zeit. angew. Chem.*, 1906, 19, 1263—1264).—The mixed salts are dissolved in water contained in a specially designed sealed tube (consisting of two separate chambers) kept at a constant temperature by means of superheated steam. The solution is effected in the one chamber and the liquid is then filtered from undissolved salts into the other chamber and slowly cooled, restored to the ordinary pressure, and then examined. P. H.

Formation of Mixed Crystals from Fused Mixtures of Lead, Silver, Thallium, and Copper Haloids. K. MÖNKE-MEYER (*Jahrb. Min. Beil.*, 1906, 22, 1—47).—The pure salts employed are found to have the following temperatures of solidification: lead chloride, 495° ; lead bromide, 370° ; lead iodide, 358° ; silver chloride, 452° ; silver bromide, 422° ; silver iodide, 552° ; thallous chloride, 426° ; thallous bromide, 450° ; thallous iodide, 431° ; cuprous chloride, 419° ; cuprous bromide, 480° ; cuprous iodide, 590° .

The liquidus and solidus curves for the various binary combinations of salts of the same metal have been determined. In the case of $\text{PbCl}_2 + \text{PbBr}_2$, it is found that a continuous series of mixed crystals is formed, and the temperatures of solidification of the mixtures lie between the temperatures of solidification of the components. In other cases ($\text{AgCl} + \text{AgBr}$, $\text{AgBr} + \text{AgI}$, $\text{TlCl} + \text{TlBr}$, $\text{TlBr} + \text{TlI}$, $\text{Cu}_2\text{Cl}_2 + \text{Cu}_2\text{Br}_2$, $\text{Cu}_2\text{Br}_2 + \text{Cu}_2\text{I}_2$), the components form a continuous series of mixed crystals, but the liquidus curve exhibits a minimum. In a third class, comprising the systems $\text{PbBr}_2 + \text{PbI}_2$, $\text{PbCl}_2 + \text{PbI}_2$, $\text{AgCl} + \text{AgI}$, $\text{TlCl} + \text{TlI}$, $\text{Cu}_2\text{Cl}_2 + \text{Cu}_2\text{I}_2$, there is a gap in the mixed crystal series, and the liquidus curve consists of two separate branches meeting at a eutectic point.

The author has studied also the transformations which the mixed crystals undergo in the various series comprising silver iodide, thallous iodide, cuprous chloride, bromide, and iodide, which are all dimorphous. In the case of the system $\text{Cu}_2\text{Br}_2 + \text{Cu}_2\text{I}_2$, the first example is found of Roozeboom's type I3 (*Abstr.*, 1900, ii, 132), in which one continuous series of mixed crystals changes to another continuous series, the curve of the transition temperatures exhibiting a minimum.

J. C. P.

Automatic Mercury Pump and Apparatus for the Study of Gases. FRANCESCO ANDERLINI (*Gazzetta*, 1906, 36, i, 458—472).—The following pieces of apparatus are described and depicted: (1) an automatic mercury pump; (2) an automatic mercury pump with multiple fall; (3) a pump for the extraction and transport of gases; (4) apparatus for distilling mercury in a vacuum; (5) apparatus for the absorption of nitrogen by means of magnesium and lime; (6) apparatus for the combustion of hydrocarbons in oxygen.

T. H. P.

High Vacua in the Scheibler Type of Desiccator. HERBERT C. GORE (*J. Amer. Chem. Soc.*, 1906, 28, 834—837).—The method described by Benedict and Manning (*Abstr.*, 1902, ii, 449) for obtaining high vacua in the Hempel desiccator has been modified for use with desiccators of the Scheibler type.

Through an aperture in the side of the desiccator a tube is inserted which on the inside reaches nearly to the cover and on the outside carries a stop-cock; the desiccator is also provided with a simple U-shaped manometer. The ether is placed in a small dish which floats on the surface of the sulphuric acid at the bottom of the desiccator. On reducing the pressure, the ether evaporates rapidly, and on closing the stop-cock the vapour is absorbed by the sulphuric acid.

Experiments are described which show that this apparatus is quite as efficient as the Hempel form.

E. G.

Inorganic Chemistry.

Function of the Catalyst in the Deacon Process for the Manufacture of Chlorine. MARIO G. LEVI and MARIO VOGHERA (*Gazzetta*, 1906, 36, i, 513—534. Compare Levi and Bettoni, *Abstr.*, 1905, ii, 515).—From the results of further experiments on the action of copper salts and other salts as catalysts in the Deacon chlorine process, the authors conclude that although there are certain facts in favour of the old fundamental hypothesis, this does not afford a sufficient explanation of the process. There are not, however, sufficient data to disprove the hypothesis. The most satisfactory hypothesis is that of a catalysis taking place by means of intermediate reactions, the intermediate products being unstable hydrates. The Deacon process is hence to be regarded as one of double catalysis, or, better, one in which two reactions occur simultaneously, one essentially catalytic in character and the other rather chemical than catalytic. T. H. P.

Preparation of Hydrogen Chloride and Bromide from their Constituent Elements. EDUARD HOPPE (D.R.-P. 166598).—The metallic chlorides or bromides having an acid reaction to litmus decompose when their aqueous solutions are boiled, and evolve hydrogen chloride

or bromide, leaving a residue of basic chloride or hydroxide. When hydrogen and chlorine in equivalent proportions are brought into contact with the basic chlorides or bromides, a reaction of the following type occurs, $\text{ZnCl} \cdot \text{OH} + \text{H} + \text{Cl} = \text{ZnCl}_2 + \text{H}_2\text{O}$, and the normal chloride or bromide is regenerated. This cycle of changes is employed in producing solutions of these halogen hydrides. The chlorides of aluminium, zinc, tin, magnesium, antimony, cadmium, bismuth, boron, iron, chromium, and manganese are suitable for this purpose, and temperatures varying from 100° to 130° are employed for the hydrolysis of the normal chlorides of these elements. The reaction may be brought about either in aqueous suspensions of the basic chlorides or in porous substances impregnated with these substances in a moist condition. G. T. M.

Purification of Water by the Simultaneous Action of Permanganates and the Electric Current. EUGÈNE PELLAS and JULIEN LEGRAND (D.R.-P. 166625).—A soluble permanganate is added to the water to be purified, and an electric current is passed through the solution for a short time. With a current density of 0.05 to 1 ampere per sq. decimetre, two to five minutes suffice to destroy the organic impurities completely. The current greatly accelerates the oxidising action of the permanganate by electrolysing this salt into free alkali and permanganic acid; the latter on oxidising the impurities becomes itself reduced to insoluble manganic hydroxide, which may be removed by filtration. G. T. M.

Influence of the Material of the Vessel and of Light on the Formation of Ozone by the Silent Discharge. FRANZ RUSS (*Zeit. Elektrochem.*, 1906, 12, 409—412).—When ozonisers of Thuringian glass and of quartz are used under the same conditions in the dark, the yield of ozone in the quartz apparatus is nearly one-half of that obtained in the glass apparatus. Exposing the glass apparatus to the light of a quartz mercury lamp reduced the yield of ozone from 7.13 per cent. to 6.7 per cent. An ozoniser of uviole glass gave 5.34 per cent. of ozone in the dark and 4.1 per cent. when exposed to the light of the mercury lamp, whilst with the quartz ozoniser the figures were 2.27 and 1.26 per cent. respectively. It appears, therefore, that the yield of ozone is worse the greater the transparency of the ozoniser for ultra-violet light. T. E.

Thermal Production of Ozone and of Nitric Oxide in moving Gases. FRANZ FISCHER and HANS MARX (*Ber.*, 1906, 39, 2557—2566. Compare Fischer and Braehmer, this vol., ii, 224).—From the results of previous experiments it is obvious that the rapid heating of air followed by rapid cooling favours the production of ozone, whereas nitric oxide alone is obtained if the heating and subsequent cooling are slowly performed. In these facts lies the key to the problem of the production of ozone in air by purely thermal means.

The flame of hydrogen burning at the end of a vertical quartz capillary tube is adjusted to a height of about 8 mm.; through a second horizontal capillary, the extremity of which nearly touches that of the vertical tube, a current of air drives the products of combustion

into a spherical glass vessel cooled externally by flowing water. The presence of hydrogen peroxide in the condensed water is detected by titanous acid, whilst the issuing gases, although having the odour of ozone, colour "tetramethyl-base paper" yellow, indicating the presence of nitric oxide. The presence of ozone, however, is detected by means of liquid air (this vol., ii, 627).

On using a current of oxygen in the place of air, ozone is detected almost at once in the issuing gases.

Ozone is not produced in recognisable quantities when air or oxygen is passed over a glowing platinum wire. This negative result is due partly to the comparatively low temperature of the wire, but mainly to the decomposing action on the ozone of the particles of platinum produced by the disintegration of the wire (compare Mulder and Meulen, Abstr., 1883, 284).

Ozone is easily detected by its odour and action on "tetramethyl-base paper" when a current of oxygen or of air, with a driving pressure of about 10 mm. of mercury, is passed over a glowing Nernst filament; when the driving force is only about 0.2—0.4 mm. of water, the paper is coloured yellow, indicating the presence of nitric oxide (compare Clement, Abstr., 1904, ii, 479; Rossi, Abstr., 1905, ii, 386).

Ozone is also produced when a glowing Nernst filament is rotated in air. C. S.

A Hydrate of Sulphur. WALTÈRE SPRING (*Rec. trav. chim.*, 1906, 25, 253—259).—The sulphur which is formed together with polythionic acids when hydrogen sulphide and sulphur dioxide react in aqueous solution is a mixture of soluble sulphur and a definite hydrate, $S_8 \cdot H_2O$, and not a new allotropic form of sulphur, "sulphur δ ," as described by Debus (*Chem. News*, 1888, 57, 87). In order to separate the hydrate from the soluble sulphur, the mixed precipitate is washed by dialysis until it is neutral to litmus, and dried in a vacuum at the ordinary temperature until the weight is constant; the yellow mass thus obtained is powdered, sifted through silk, again dried in a vacuum, and finally extracted with carbon disulphide, which dissolves 51.6 per cent. of the total mass. The residual *sulphur hydrate*, $S_8 \cdot H_2O$, when compressed into cylinders, has a sp. gr. 1.9385 at $19^\circ/4^\circ$, loses its water at 80° , and has a slight vapour pressure at the ordinary temperature, the powdered substance losing 2.41 per cent. and the compressed substance 1.33 per cent. when kept over sulphuric acid for 205 days. The partially dried powder contains 3.1 per cent. and the compressed substance 5.8 per cent. of sulphur soluble in carbon disulphide. If, however, the hydrate consisted of octahedral sulphur combined with water, the amount of soluble sulphur in the partially dried powder would be 35.186 per cent.; it is probable, therefore, that the hydrate is derived from an amorphous unstable variety of sulphur which is transformed slowly under ordinary conditions, and more rapidly under pressure, into soluble sulphur. M. A. W.

Action of Sulphur on Solutions of Metallic Salts. ANTONIO MANUELLI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 703).—When a cupric chloride solution, acidified with hydrochloric acid, is heated

with sulphur in a sealed tube at 150—180°, part of the cupric chloride is converted into the cuprous salt. Under similar conditions, potassium dichromate is reduced to chromium sesquioxide. In both cases, there is abundant formation of sulphuric acid in the solution. T. H. P.

Ions derived from Sulphur and Complex Ions containing Mercury. JOSEPH KNOX (*Zeit. Elektrochem.*, 1906, 12, 477—481).—The solubility of mercury sulphide in solutions of sodium sulphide at 25° is given in the following table:

Conc. Na ₂ S, mols./litre.	Red HgS, mols./litre.	Black HgS, mols./litre.
2.03	1.144	—
1.52	0.7832	0.8561
1.015	0.4423	0.5002
0.755	0.2878	0.3336
0.5	0.1500	0.1805
0.25	0.04544	0.05622
0.10	0.00824	0.01085

The change of the black sulphide into the red form is rapid only in presence of very concentrated solutions of sodium sulphide. In the more concentrated solutions used it is possible that the observed solubility of the black sulphide was too low owing to a partial change into the red form. The solubility diminishes slowly as the temperature rises. It is probable that the dissolution of mercuric sulphide is due to S'' ions, and that the hydrolysis of the sodium sulphide ($\text{Na}_2\text{S} + \text{H}_2\text{O} \rightleftharpoons \text{NaOH} + \text{NaHS}$ or $\text{S}'' + \text{H}_2\text{O} \rightleftharpoons \text{HS}' + \text{OH}'$) by diminishing the concentration of these ions diminishes the solubility. In agreement with this view, it is found that the addition of sodium hydroxide increases the solubility. In a concentrated solution of sodium hydroxide, very nearly one molecule of mercuric sulphide dissolves for each molecule of sodium sulphide present, which would point to the formula Na_2HgS_2 for the complex salt in solution.

By applying the method devised by Bodländer (*Abstr.*, 1902, ii, 63), it is found that the ions of the complex salt contain one atom of mercury.

Assuming that the formula Na_2HgS_2 is correct, it is easily shown that in solutions saturated with mercuric sulphide the product of the concentrations of the mercury (Hg'') and complex (HgS_2'') ions must be constant. Measurements of the concentration of the Hg'' ions, made by means of concentration cells, showed that this is the case. The concentrations of the Hg'' ions in the solutions of the red sulphide tabulated above varied from 3.53×10^{-53} to 300×10^{-53} . The results are used to calculate the values of certain equilibrium constants; the probable values found are: $[\text{OH}'][\text{HS}']/[\text{S}''] = 10$ and $[\text{H}'][\text{S}'']/[\text{HS}'] = 1.2 \times 10^{-15}$. By means of these values and the known dissociation constants of water and hydrogen sulphide, it is possible to calculate the concentrations of the S'' or SH' ions in aqueous solutions of sulphides. The concentration of the S'' ions, on which the precipitation of metallic sulphides depends, varies, for example, from 0.09 mol. per litre in a normal solution of sodium

sulphide to 1.1×10^{-23} mols. per litre in normal hydrochloric acid saturated with hydrogen sulphide. T. E.

Modified Hydrogen Sulphide Generator. A. W. BROWNE and M. F. MEHLING (*J. Amer. Chem. Soc.*, 1906, 28, 838—843).—Certain modifications of the Ostwald gas generator are described which effect the following advantages. The variations in pressure which are noticed with the Ostwald apparatus are obviated, and the gas is evolved at a uniform pressure so long as the rate of consumption does not exceed the maximum rate of generation of which the apparatus is capable. The spent acid, when completely neutralised, is automatically discharged without altering the pressure in the apparatus. Another difficulty which is encountered with the Ostwald apparatus is the formation of channels through the solid ferrous sulphide by the constant dropping of the acid on one spot. This has been overcome by a device consisting of a double dropper. The apparatus requires very little attention, is easily constructed, and is suitable for the use of large classes. For details, the description and diagram in the original must be consulted. E. G.

Isolation of Pure Selenium from the Residues of the Lead Chamber. HERMANN KOCH (D.R.-P. 167457).—The residues of the lead chamber yield pure selenium when mixed into a paste with sulphuric acid of moderate concentration and treated at 50—60° with potassium permanganate, the dry salt being carefully strewn over the surface of the mixture, which is thoroughly stirred during the operation. The oxidation, which takes place in the following manner, $4\text{KMnO}_4 + 5\text{Se} + 6\text{H}_2\text{SO}_4 = 2\text{K}_2\text{SO}_4 + 4\text{MnSO}_4 + 5\text{SeO}_2 + 6\text{H}_2\text{O}$, is complete when the solid residue becomes white, whilst the acid liquid is red. Sodium chloride is then added to precipitate any silver which may be present and the mixture is diluted and filtered, the selenium being precipitated from the acidified filtrate by means of sulphurous acid. About 80 per cent. of the total selenium may thus be isolated. G. T. M.

Isomorphism of Tellurium and Selenium. GIOVANNI PELLINI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 629—637, 711—714).—The author has studied the solubility of mixed crystals of TeBr_2Ph_2 and SeBr_2Ph_2 . The former of these compounds is dimorphous, crystallising from carbon disulphide in the tetragonal system and from benzene in the triclinic system, but the latter crystallises from either of these solvents in the rhombic system.

Cold saturated solutions of the two compounds were mixed in different proportions, and the mixed solutions allowed to evaporate in a thermostat at 21°. In this way mixed crystals of two distinct types were obtained: (1) triclinic crystals containing from 0 to 51.18 molecules per cent. of the selenium compound, and (2) rhombic crystals containing from 94.25 to 100 per cent. of the selenium compound. The case is hence one of isodimorphism.

By mixing nearly saturated aqueous solutions of rubidium hydrogen tellurate and rubidium hydrogen selenate in various proportions and

evaporating the mixed solutions at 50—80° until they deposited crystals on cooling, the author has obtained mixed crystals of the two salts containing from 42 to 53 mols. per cent. of the selenate (compare Norris and Kingman, *Abstr.*, 1902, ii, 15). T. H. P.

Borates. M. DUKELSKI (*Zeit. anorg. Chem.*, 1906, 50, 38—48. Compare Atterberg, this vol., ii, 281).—The equilibrium in the system potassium hydroxide—boric acid—water and in the corresponding system with sodium hydroxide has been investigated at 30°. The composition of both liquid and solid phases was determined by Schreinemaker's residue method, for which it is not necessary to isolate the solid phase, and the results are represented on the usual triangular diagram. Under the given conditions, the following potassium compounds exist in the solid state: $K_2O, B_2O_3, 2\frac{1}{2}H_2O$; $K_2O, 2B_2O_3, 4H_2O$; and $K_2O, 5B_2O_3, 8H_2O$, whilst there are four solid sodium compounds with the respective formulæ: $Na_2O, B_2O_3, 4H_2O$; $Na_2O, B_2O_3, 8H_2O$; $Na_2O, 2B_2O_3, 10H_2O$; and $Na_2O, 5B_2O_3, 10H_2O$. It is probable that other compounds exist under different temperature conditions, and the investigation is being continued in this direction. G. S.

The Diamond Problem. ADOLF KOENIG (*Zeit. Elektrochem.*, 1906, 12, 441—444).—After an historical account of the methods which have been proposed for the preparation of diamond, experiments are described, the object of which was to deposit carbon from carbon monoxide, using diamond as catalyst. A diamond was heated in a porcelain tube in a current of pure carbon monoxide; up to 1000° no reaction occurred, at 1250° a ring of black carbon was deposited on the porcelain tube, but the diamond remained entirely unchanged. Apparently the catalytic action of the porcelain was greater than that of the diamond. T. E.

Measurement of Temperature in the Formation of Carborundum. SAMUEL A. TUCKER and ALEXANDER LAMPEN (*J. Amer. Chem. Soc.*, 1906, 28, 853—858).—The experiments described were carried out with an electric furnace constructed on the lines of a commercial carborundum furnace. It was provided with a horizontal graphite tube passing through the centre and containing a plug which could be moved to any desired section, and its temperature measured by means of an optical pyrometer. The apparatus and method of working are described with the aid of diagrams.

After an experiment had been made and the furnace had cooled, a section was made exposing the graphite tube. By examining the different layers formed it was found possible to construct a curve which combines the temperature measurements with the measurements defining the limits of the products (graphite, carborundum, and siloxicon). The average of the results gives 2220° as the decomposition temperature of carborundum into graphite and silicon, and 1950° as its temperature of formation (that is, the temperature at which the amorphous compound changes into the crystalline form). E. G.

Rate of Reaction in Fused Silicates. CORNELIO DOELTER (*Zeit. Elektrochem.*, 1906, 12, 413—414).—The more complex silicates are usually very viscous when fused and their rate of crystallisation is extremely small. Decomposition into simpler constituents usually accompanies fusion, and owing to the small rate of crystallisation the original compound does not separate from the melt, the simpler compounds crystallising more rapidly. Garnet, for example, decomposes into the compounds Ca_2SiO_4 and $\text{CaAl}_2\text{Si}_2\text{O}_8$, which crystallise out instead of the original garnet. Many other apparently anomalous phenomena in fused silicates are explicable by the small rate of reaction.

T. E.

Production of Alkali Nitrites. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 168272).—When a mixture of ammonia and air or oxygen is passed over certain oxides of the heavy metals at about 650° , the ammonia is oxidised exclusively to nitrous acid. A large excess of air is required, the gaseous mixture containing only 4—5 per cent. by volume of ammonia. When this reaction is carried out with ferric oxide at 700° , a continuous current of nitrous gas is produced, which may be absorbed by aqueous sodium hydroxide or carbonate.

G. T. M.

Sulphides of Rubidium and Cæsium. WILHELM BILTZ and ERNST WILKE-DÖRFURT (*Zeit. anorg. Chem.*, 1906, 50, 67—81. Compare Abstr., 1905, ii, 162; this vol., ii, 283).—In former papers it has been shown that the sulphides of rubidium and cæsium may be represented by the general formula M_2S_n , where n denotes the whole numbers from 1 to 6, and the mono-, tetra-, and penta-sulphides have been isolated. In the present paper, the isolation of the di- and tri-sulphides is described, and an account is given of their properties.

When the pentasulphides are heated in a current of hydrogen, the rate of evolution of sulphur becomes very slow at points corresponding with the composition of the disulphides, but the results are somewhat complicated by the volatility of the latter compounds themselves. On solution and recrystallisation of the residues, however, the pure disulphides are obtained.

Rubidium disulphide, $\text{Rb}_2\text{S}_2 \cdot \text{H}_2\text{O}$, occurs in lustrous, colourless crystals, which dissolve to a colourless solution in water and become dark red on heating. *Cæsium disulphide*, $\text{Cs}_2\text{S}_2 \cdot \text{H}_2\text{O}$, resembles in all respects the corresponding rubidium salt. The anhydrous sulphides are dark red.

When, on the other hand, the pentasulphides are heated in a current of nitrogen, the rate of evolution of sulphur diminishes at points corresponding with the composition of the trisulphides, and on dissolving the residues and recrystallising, the latter compounds are obtained in a pure state.

Rubidium trisulphide, $\text{Rb}_2\text{S}_3 \cdot \text{H}_2\text{O}$, forms yellow, lustrous leaflets; the corresponding *cæsium* compound, $\text{Cs}_2\text{S}_3 \cdot \text{H}_2\text{O}$, also occurs in yellow leaflets. The latter compound was also obtained in the anhydrous form in red leaflets.

The rubidium sulphides are much less hygroscopic than those of

cæsium. Further, cæsium disulphide is more volatile than the corresponding rubidium salt.

The paper concludes with a summary of the methods of preparation and properties of all the sulphides referred to in the three papers.

G. S.

Rate of Autoracemisation of Optically Active Ammonium Salts. HANS GOLDSCHMIDT (*Zeit. Elektrochem.*, 1906, 12, 416—418).—In the reversible conversion of an active substance into its optically opposite modification, the velocity constants of the two reactions are equal, hence the equation $dx/dt = k(a - x) - k'x$ becomes $dx/dt = k(a - 2x)$. The rotatory power of the solution is, however, a measure of $a - 2x$, because each dextrorotatory molecule which disappears gives rise to a lævorotatory molecule. Hence the conclusion drawn by Wedekind (this vol., i, 419) is correct apart from any hypothesis as to the mechanism of the change. It is also shown that when no racemic compound is formed the free energy of the change of any optically active substance into the racemic modification is $2RT \log 2$ per molecule and that the partial vapour pressure of each constituent in the racemic mixture is one-half its vapour pressure in the free state. Hence it is impossible to separate such a mixture by processes such as freezing or evaporation. The possibility of such a separation would indicate the presence of a racemic compound.

T. E.

Higher Forms of Combination of Silver. G. A. BARBIERI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 500—504).—According to several observers, electrolysis of a neutral solution of silver nitrate leads to the deposition on the anode of a peroxide of silver which contains a higher proportion of oxygen than Ag_2O_2 , and which gradually decomposes into the latter and oxygen at the ordinary temperature.

The position of silver in the periodic system of the elements between copper and gold would render possible the existence of a compound of the formula Ag_2O_3 , which would be intermediate in stability between the corresponding copper and gold compounds.

On mixing a concentrated nitric acid solution of this superoxide with aqueous potassium permanganate, the solution acquires a reddish-brown colour, which, on the gradual addition of dilute hydrogen peroxide solution, changes to the characteristic violet colour of permanganate. Cerous salts are immediately reduced in the cold by a nitric acid solution of the superoxide, which is, however, not reduced by lead or manganese dioxide.

The superoxide is hence, according to Piccini's rule, not a true peroxide, but a higher oxide of silver. In its behaviour towards hydrogen peroxide and cerous salts, and also in possessing metallic conductivity, it exhibits a close analogy with lead dioxide.

On electrolysing a cold saturated solution of potassium hydrogen carbonate, using silver electrodes, the anode becomes at first covered with a layer of black oxide, and thus, gradually passing into solution, gives to the anodic liquid a reddish-brown colour. This colour disappears slowly if the current is stopped or instantaneously on

addition of ammonia, hydrogen peroxide, or a reducing agent such as a salt of hydrazine or hydroxylamine. A solution with the same colour and other properties as the above may be more readily obtained by heating a solution of silver carbonate in potassium hydrogen carbonate with potassium persulphate. A more stable solution, which can be kept for several weeks in the dark, may be prepared from sodium pyrophosphate, silver nitrate, and potassium persulphate.

In these reddish-brown solutions, the silver exists in a highly oxidised condition and is capable of oxidising ferrous or cobaltous salts.

T. H. P.

Estimation of the Atomic Weight of Copper. ERNST MURMANN (*Monatsh.*, 1906, 27, 351—361. Compare Abstr., 1897, ii, 346).—The author has determined the atomic weight of copper by alternate reduction and oxidation of the pure copper previously described (*loc. cit.*). As a porcelain crucible alters in weight on prolonged heating over a Bunsen flame, the copper was heated in a double crucible. The variations in the results obtained, 63.513—64.153 ($O=16$), are consequent probably on the absorption of air by the porous reduced copper. The author discusses the results and deduces the most probable value for the atomic weight of copper as 63.53 ± 0.03 .

G. Y.

Effect of Certain Elements on the Structure and Properties of Copper. ARTHUR H. HIORNS (*J. Soc. Chem. Ind.*, 1906, 25, 616—624).—For details of the results obtained, the original paper should be consulted, but the main conclusions arrived at are that the malleability of copper is scarcely affected by the addition of small quantities of phosphorus, is slightly diminished by arsenic, and still more so by antimony. Lead renders copper imperfectly malleable, whilst bismuth makes it quite unworkable. Arsenic or antimony added to copper containing lead or bismuth diminishes the brittleness caused by the lead or bismuth.

P. H.

Action of Iodine on Mercurous and Mercuric Sulphates. KAMILLO BRUECKNER (*Monatsh.*, 1906, 27, 341—349).—When powdered together and carefully heated over a free flame in the proportion $6\text{Hg}_2\text{O}:12\text{I}_2$, mercurous oxide and iodine form mercuric iodide and iodate, which can be separated by means of absolute alcohol; the reaction takes place slowly at the ordinary temperature in presence of water, more quickly on boiling with water, but only extremely slowly in presence of alcohol. The same products are formed by the interaction of mercuric oxide and iodine ($6\text{HgO}:6\text{I}_2$) when heated, or in water at the ordinary temperature; the reaction takes place only slowly in alcoholic solution, aldehyde being formed.

The interaction of anhydrous mercurous sulphate and iodine at high temperatures leads to the formation of mercuric iodide, mercuric sulphate, and free sulphuric acid. In water, the products of the reaction are mercuric iodide and iodate and sulphuric acid; if alcohol is present, it is oxidised partially to aldehyde.

When heated, mercuric sulphate and iodine interact only to a small extent, which is dependent probably on the decomposition of the

sulphate, but in presence of water they yield products varying with the order and proportion of mixing. The yellow basic sulphate formed by adding a small amount of water to mercuric sulphate reacts with iodine slowly, forming a white mass; this is decomposed by excess of water in a complicated manner. A similar white substance is formed by grinding mercuric sulphate with mercuric iodide or with iodine and a small amount of water (compare Ditte, *Abstr.*, 1905, ii, 391). If mercuric sulphate and iodine are ground together and much water added, the product contains mercuric iodide and iodate. In presence of alcohol, mercuric sulphate and iodine form mercuric iodide and iodate and sulphur trioxide, the alcohol being oxidised to aldehyde. G. Y.

Preparation of a Basic Aluminium Sulphate. PETER SPENCE & Co. (D.R.-P. 167419).—A crystalline basic aluminium sulphate, $\text{Al}_2\text{O}_3 \cdot 2\text{SO}_3$, may be prepared by heating an excess of alumina with sulphuric acid, sp. gr. 1.475, in an autoclave, and treating the solution with a sufficient amount of calcium carbonate or hydroxide to increase the basicity of the sulphate to about 20 to 28 per cent. calculated on the amount of alumina required to form the normal sulphate. The clear solution after this treatment is evaporated under reduced pressure until the crystals of the basic sulphate begin to separate.

G. T. M.

Chemistry of Iron. HANNS VON JÜPTNER (*Ber.*, 1906, 39, 2376—2402).—A lecture delivered before the German Chemical Society.

G. Y.

Silicon Compounds of Iron. Formation of Silicides in the Electric Furnace. B. L. VANZETTI (*Gazzetta*, 1906, 36, i, 498—513).—In the interior of the silicious mass obtained from an electric furnace in which coke, sand, and lime were heated together at a temperature of about 3000° , the author found metallic buttons having the sp. gr. 5.76—6.29, a hardness of about 7 on Mohr's scale, and the composition FeSi . The chemical characters of the substance point to its being a chemical individual, as also does the absence of magnetic properties. The iron, which occurs to the extent of 3 per cent. of ferric oxide in the coke, doubtless combines firstly with carbon, the latter being subsequently displaced by silicon formed by reduction of the silica present.

Similar experiments at a higher temperature than 3000° yielded masses varying in appearance and sp. gr. (3.46—5.54) and more readily acted on by reagents than FeSi . One of the buttons had a sp. gr. approximately equal to that of FeSi_2 , but its composition did not correspond with this formula.

T. H. P.

Co-ordination-isomerism and Polymerism among the Chromium Salts. PAUL PFEIFFER (*Annalen*, 1906, 346, 28—81. Compare *Abstr.*, 1905, i, 33, and this vol., i, 71).—By co-ordination-isomerism is understood the isomerism which arises from the union of

complex ions. In the first case, the negative radicle of such a pair of isomeric salts is combined with one of the so-called "central-atoms" in one isomeride, whilst in the other, another atom has become the "central-atom," a change in valency at the same time taking place, thus: $[\text{Pt}''(\text{NH}_3)_4], \text{Pt}^{\text{IV}}\text{Cl}_6$ is isomeric with $[\text{Pt}^{\text{IV}}\text{Cl}_2(\text{NH}_3)_4], \text{Pt}''\text{Cl}_4$. In the second case, which is the more common, the groups of the complex ions mutually replace one another, thus:

$[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$

and $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2][\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$ or $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$ and $[\text{CuCl}_4][\text{Pt}(\text{NH}_3)_4]$. The replacement of one group by the other in the complex ions of the co-ordination-isomerides brings about a change of valency in the ion, the valency finally becoming nil; thus: $[\text{Co}(\text{NH}_3)_6]^{+3}[\text{Co}(\text{NO}_2)_6]^{-3}$; $[\text{Co}(\text{NH}_3)_5(\text{NO})]^{+4}[\text{Co}(\text{NH}_3)(\text{NO}_2)_5]^{-4}$; $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^{+4}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^{-4}$; and $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]^{+0}[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]^{-0}$. The molecular formula of the last compound is only half that given; the other compounds are polymerides.

Co-ordination-isomerism is well shown among the oxalo-cobalt and -chromium salts, which have an analogous constitution to the salts $[\text{Cr en}_3][\text{Cr}(\text{C}_2\text{O}_4)_3]$ (greyish-green) and $[\text{Cr en}_2(\text{C}_2\text{O}_4)][\text{Cr en}(\text{C}_2\text{O}_4)]$ (red) (en = ethylenediamine) (*loc. cit.*), the group NH_3 taking the place of the group en. Thus the salt $[\text{Cr}(\text{NH}_3)_6][\text{Cr}(\text{C}_2\text{O}_4)_3]$ is green and yields with hydrogen bromide a hexamminechromium bromide, whilst the salt $[\text{Cr}(\text{NH}_3)_4(\text{C}_2\text{O}_4)][\text{Cr}(\text{NH}_3)_2(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$ is red and gives with nitric acid the *nitrate*, $[\text{Cr}(\text{NH}_3)_4(\text{C}_2\text{O}_4)]\text{NO}_3$. These compounds are related to the chromium-cobalt salts, $\text{CrCo}(\text{C}_2\text{O}_4)_3 \cdot 6\text{a}$ (a = co-ordinative univalent groups), for example: $[\text{Cr en}_3][\text{Cr}(\text{C}_2\text{O}_4)_3]$; $[\text{Cr en}_2(\text{C}_2\text{O}_4)][\text{Co en}(\text{C}_2\text{O}_4)_3]$; $[\text{Cr en}(\text{C}_2\text{O}_4)_2][\text{Co en}_2(\text{C}_2\text{O}_4)]$; $[\text{Cr}_2(\text{C}_2\text{O}_4)_3][\text{Co en}_2]$.

In the order just given, the colour of these salts passes from green through red to brown. Their constitution was arrived at by decomposition with hydrobromic acid. In no case was a transformation of one isomeride into another observed. Analogous salts in which ammonia or propylenediamine takes the place of ethylenediamine have been prepared. It is noted that the colour of the salts $[\text{Cr}(\text{NH}_3)_6][\text{Cr}(\text{C}_2\text{O}_4)_3]$ and $[\text{Cr en}_3][\text{Cr}(\text{C}_2\text{O}_4)_3]$ is affected by the nature of the illumination; in daylight they are green or greyish-green, but in electric light appear brown.

The corresponding chromium-cobalt cyano-salts, originally prepared by Jörgensen and Braun, have been investigated, and their constitution fixed by means of their reaction with silver nitrate.

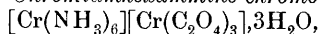
In the case of the thiocyno-compounds, two stereoisomeric salts have been observed, together with a third which appears to be polymeric. They are flesh-coloured, insoluble powders, and react characteristically with chlorine, their constitution being thus determined. They are formed in the following reactions: $[\text{Cr en}_3]\text{Cl}_3 + [\text{Cr}(\text{SCN})_6]\text{K}_3 = 3\text{KCl} + [\text{Cr en}_3][\text{Cr}(\text{SCN})_6] = \text{Cr}_2 \text{ en}_6(\text{SCN})_6$; $3[\text{Cr en}_2(\text{SCN})_2]\text{Cl} + [\text{Cr}(\text{SCN})_6]\text{K}_3 = 3\text{KCl} + [\text{Cr en}_2(\text{SCN})_2]_3[\text{Cr}(\text{SCN})_6] = \text{Cr}_4 \text{ en}_6(\text{SCN})_{12}$, a cis- or trans-compound.

A number of triethylenediamine- and tripropylenediamine-cobalt salts were prepared from chloropentamminecobalt chloride and ethylene-

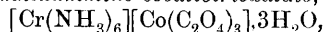
or propylene-diamine monohydrate, ammonia being evolved and a yellow base formed, from which the salts can be obtained.

The following hitherto unknown salts have been prepared :

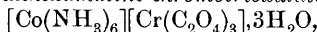
[With S. BASCI.]—*Chromiumhexammine chromotrioxalate*,



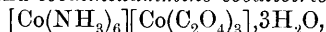
crystallises in dark green leaflets; *chromiumoxalatetrammine diammine-chromodioxalate*, $[\text{Cr}(\text{NH}_3)_4(\text{C}_2\text{O}_4)][\text{Cr}(\text{NH}_3)_2(\text{C}_2\text{O}_4)_2]\cdot 3\text{H}_2\text{O}$, in orange-red scales; *chromiumhexammine cobaltotrioxalate*,



in green leaflets; *cobalthexammine chromotrioxalate*,

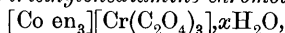


in brown leaflets; and *cobalthexammine cobaltotrioxalate*,



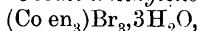
is a green, crystalline powder.

[With A. TRIESCHMANN.]—*Chromiumtriethylenediamine cobaltotrioxalate*, $[\text{Cr en}_3][\text{Co}(\text{C}_2\text{O}_4)_3]$, is a grass-green precipitate; *cobalt-triethylenediamine chromotrioxalate*, $[\text{Co en}_3][\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot 6\text{H}_2\text{O}$, a brown, crystalline precipitate; *cobaltoxalodiethylenediamine chromoethylenediaminedioxalate*, $[\text{Co en}_2(\text{C}_2\text{O}_4)][\text{Cr en}(\text{C}_2\text{O}_4)_2]\cdot 2\text{H}_2\text{O}$, a red, crystalline precipitate, and *cobalt-triethylenediamine chromotrioxalate*,

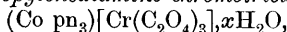


a grass-green, crystalline precipitate.

[With TH. GASSMANN.]—*Cobalt-triethylenediamine bromide*,

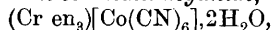


crystallises in yellow needles, the *iodide* (with H_2O) forms yellow crystals, and the *thiocyanate*, which is anhydrous, dark yellow crystals. *Cobalt-tripropylenediamine chloride*, $(\text{Co pn}_3)\text{Cl}_3\cdot \text{H}_2\text{O}$, is a yellow, crystalline powder, whilst the *bromide* and *iodide* (with H_2O) form yellow needles; the anhydrous *thiocyanate* is a pale yellow precipitate, and the *nitrate* crystallises in yellow needles. *Cobalt-tripropylenediamine cobaltihexacyanide*, $(\text{Co pn}_3)[\text{Co}(\text{CN})_6]\cdot 2\text{H}_2\text{O}$, crystallises in yellow needles, and the corresponding *ferricyanide*, $(\text{Co pn}_3)[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$, reddish-yellow needles. *Cobalt-tripropylenediamine chromotrioxalate*,



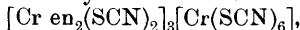
is a chocolate-coloured, crystalline precipitate, whilst the isomeric *chromium cobaltitrioxalate*, $(\text{Cr pn}_3)[\text{Co}(\text{C}_2\text{O}_4)_3]\cdot x\text{H}_2\text{O}$, is a green powder.

[With M. HAIMANN.]—*Chromiumhexammine cobaltihexacyanide*, $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$, crystallises in yellow needles, and the isomeric *cobalthexammine chromihexacyanide*, $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$, in needles. *Chromiumtriethylenediamine cobaltihexacyanide*,



crystallises in yellow leaflets, and *cobalt triethylenediamine chromihexacyanide*, $(\text{Co en}_3)[\text{Cr}(\text{CN})_6]\cdot 2\text{H}_2\text{O}$, in dark yellow needles. *Chromium-tripropylenediamine cobaltihexacyanide*, $(\text{Cr pn}_3)[\text{Co}(\text{CN})_6]\cdot x\text{H}_2\text{O}$, is a powder, whilst the isomeric *cobalt-tripropylenediamine chromihexacyanide* crystallises with $3\text{H}_2\text{O}$. *Chromiumtriethylenediamine chromihexathiocyanate*, $(\text{Cr en}_3)[\text{Cr}(\text{SCN})_6]$, is a flesh-coloured precipitate.

Chromiumdithiocyanodiethylenediamine chromihexathiocyanate,



exists in two isomeric modifications, a cis- and a trans form.

K. J. P. O.

Attempt to prove the Existence of Chromic Acids by means of the Electrical Conductivity. TULLIO COSTA (*Gazzetta*, 1906, 36, i, 535—540).—Ebullioscopic measurements of chromic acid in aqueous solution show that solutions not too concentrated when heated at 100° contain the acid $\text{H}_2\text{Cr}_2\text{O}_7$ and not H_2CrO_4 . This result confirms that arrived at by cryoscopic measurements (Ostwald, Abstr., 1888, 1009).

Further, a solution of chromic acid prepared by Moissan's method (Abstr., 1884, 1267) has the same electrical conductivity when cooled to 0° either directly or after heating to 100°, so that, even by the latter treatment, no H_2CrO_4 is formed in solution. T. H. P.

Chromic Acid as an Oxidising Agent. I. KARL SEUBERT and J. CARSTENS (*Zeit. anorg. Chem.*, 1906, 50, 53—66).—The majority of the experiments were made with very dilute solutions of chromic acid, potassium iodide, and hydrochloric acid, the iodine set free after a definite interval, usually ten minutes, being titrated in the usual way. By using Ostwald's "isolation" method (the other substances being used in considerable excess) it is shown in three series of experiments that the reaction velocity is proportional to the concentrations of chromic acid, iodine ion, and hydrogen ion respectively, so that the reaction is termolecular.

In attempting to formulate the mechanism of the reaction, considerable uncertainty arises from the fact that the constitution of solutions of chromic acid is not thoroughly understood. According to Abegg and Cox (Abstr., 1904, ii, 662), $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} ions are present, as well as undissociated CrO_3 molecules. On this basis it is suggested that the time reaction may be that represented by the equation $\text{CrO}_3 + \text{H}^+ + \text{I}^- = \text{CrO}_2\text{I}\cdot\text{OH}$, followed by a rapid reaction in which the latter compound enters into double decomposition with hydriodic acid to produce iodine, water, and a chromic salt. Alternative schemes, which are also in accord with the experimental facts, are suggested.

G. S.

Electrolytic Preparation of Vanadous Salts and Properties of Vanadous and Vanadic Salts. LUIGI MARINO (*Zeit. anorg. Chem.*, 1906, 50, 49—52. Compare Piccini and Marino, Abstr., 1902, ii, 663).—In a recent paper, Rutter (this vol., ii, 366) has recommended a mercury cathode for the reduction of vanadic acid to vanadous salts instead of the platinum cathode employed by the author, but the latter now points out that in sulphuric acid solution under suitable conditions the reduction proceeds rapidly at a platinum cathode and the yield is very good. The results are not so favourable in hydrogen chloride or in neutral solution, owing, in the latter case, to formation of oxy-salts. Rutter recommends the reducing action on silver sulphate solution as a test for vanadous salts, but it is now shown that this test is not conclusive, as vanadic salts also give a precipitate with silver sulphate, being transformed to quinquevalent vanadium. The copper test already recommended by the author is not open to this objection, and possesses the additional advantage of being practically quantitative. Further, the copper test is only slightly less sensitive than the silver test. G. S.

Action of Hydrogen Peroxide on Bismuth Salts. L. MOSER (*Zeit. anorg. Chem.*, 1906, 50, 33—37).—When a solution of bismuth nitrate, acidified with nitric acid, is added slowly to a 3 per cent. solution of hydrogen peroxide mixed with a large volume of strong solution of ammonia, the dark yellow precipitate which is at first produced soon becomes a paler yellow and oxygen is evolved rapidly. The washed and dried precipitate has the approximate composition $\text{BiO}\cdot\text{OH}$, and a small quantity of basic nitrate is also present, but no higher oxide of bismuth. The author considers that the peroxide first produced, perhaps Bi_2O_4 , is completely decomposed by interaction with hydrogen peroxide according to the equation $\text{Bi}_2\text{O}_4 + \text{H}_2\text{O}_2 = \text{Bi}_2\text{O}_3 + \text{H}_2\text{O} + \text{O}_2$.
G. S.

History of Colloidal Gold. LUDWIG VANINO (*J. pr. Chem.*, 1906, [ii], 73, 575—576. Compare Vanino and Hartl, this vol., ii, 367).—The author draws attention to descriptions of colloidal gold occurring in early chemical literature, and to its supposed medicinal effects.
G. Y.

Preparation of Hydroxyloplatidiammine Sulphate. NAZARENO TARUGI (*Gazzetta*, 1906, 36, i, 364—366).—A quantitative yield of hydroxyloplatidiammine sulphate may be easily obtained as follows. Excess of a strongly ammoniacal solution of ammonium persulphate is added to aqueous platinic chloride and the liquid heated, when the yellow, crystalline precipitate formed in the cold re-dissolves. When maintained for some time at near its boiling point, the solution deposits the hydroxyloplatidiammine sulphate as a white, flocculent precipitate, which only requires filtering, washing until neutral and free from chloride, and drying.
T. H. P.

Mineralogical Chemistry.

Crystals of Sulphur from the Deposits of Miera and Valea-Sărei (Roumania). TH. NICOLAU (*Ann. Sci. Univ. Jassy*, 1906, 4, 72—74).—The angles of a number of octahedral crystals from the districts indicated in the title have been measured, and the results are given in tabular form. G. S.

Gases present in Rock-salt and in the Mud Volcanoes of Roumania. N. COSTACHESCU (*Ann. Sci. Univ. Jassy*, 1906, 4, 3—59).—The gases occluded in the rock-salt deposits and those escaping from mud volcanoes in many different districts of Roumania have been examined. To obtain the gases from rock-salt without access of air blocks of the material are dissolved in boiling air free water and the evolved gas collected over mercury. A method of obtaining the gas by grinding the rock-salt under mercury is also

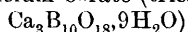
described. As regards the gases from salt, the analytical results show that there are great differences both in the mode of distribution and in the composition of the gas, and that there is no relation between the quantity of gas and the foreign matter in the salt. As regards composition, the gases may be roughly divided into two classes: (a) those containing 5—30 per cent. of nitrogen and a large quantity of methane; (b) those which are largely composed of nitrogen, some containing as much as 92 per cent. A typical example of the first class had the following composition: methane 82, ethane 9.8, olefines 1.26 per cent., and small amounts of oxygen and nitrogen. A mixture belonging to the second class contained methane 0.8, ethane 1.55, oxygen 7.5, and nitrogen 90 per cent. The gases are practically free from carbon dioxide; there is no petroleum or higher members of the olefine series; and there is no constant relation between the amounts of nitrogen and oxygen. The nitrogen is free from argon.

The gases from mud volcanoes are of corresponding composition, and probably of similar origin, to the mixtures occluded in rock-salt, the only important difference being that the former contain considerably more carbon dioxide.

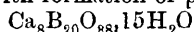
The question as to the origin of the gases is discussed, and reasons are given for supposing that they arise from the slow decay of marine fauna brought into the lagoons where the salt has deposited. It is considered that the variations in composition arise from fluctuations in the amount of the marine organisms.

The results obtained by other observers who have investigated natural gases are fully discussed and a bibliography is added. G. S.

Formation of Oceanic Salt Deposits. XLVIII. Limit of Existence and Decomposition of Boronatrocalcite; Tricalcium Pentaborate and the Artificial Production of Pandermite. JACOBUS H. VAN'T HOFF (*Sitzungsber. K. Akad. Wiss. Berlin*, 1906, 566—574. Compare this vol., ii, 456).—Boronatrocalcite does not exist at 83°, the higher limit of temperature at which a detailed examination of the formation of the salt deposits has been carried out. It breaks up at a lower temperature, according to the equation $2\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O} = \text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O} + \text{Ca}_2\text{B}_6\text{O}_{11} \cdot 7\text{H}_2\text{O} + 4\text{H}_2\text{O}$. The exact temperature at which this takes place has not been determined, for another calcium borate (tricalciumpentaborate,



is formed and lowers the temperature at which this transformation proceeds. The transition temperature in presence of the tricalcium pentaborate is below 85°, and since the presence of sodium chloride lowers such temperatures on the average to the extent of 20°, boronatrocalcite cannot exist above 65°, a conclusion which is supported by direct experiment with a dilatometer. The reverse formation of boronatrocalcite can be observed if the reacting mixture is well stirred. The conditions of existence of natroborocalcite at 25° are shown by means of a diagram. When heated to the boiling point with a solution saturated with regard to sodium and potassium chloride, boronatrocalcite decomposes with formation of pandermite,



The product, which, after remaining in contact with the solution for a few days, forms well-developed crystals, corresponds very closely with the formula given.

H. M. D.

Crystalline Form and Deformation of Bischofite and Related Chlorides of Cobalt and Nickel. OTTO MÜGGE (*Jahrb. Min.*, 1906, i, 91—112).—Natural crystals of bischofite, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, have not previously been measured: crystals from Vienenburg, in Hanover, are monoclinic [$a:b:c=1.3872:1:0.8543$; $\beta=93^\circ 42'$]. The crystals are readily deformed by gliding along the prism planes {110}. The corresponding cobalt and nickel salts are not isomorphous with bischofite; the crystallographic constants are: for $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ [$a:b:c=1.4573:1:0.9445$; $\beta=57^\circ 46'$]; for $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ [$a:b:c=1.4792:1:0.9468$; $\beta=57^\circ 58'$]. Crystals of these are also readily deformed, but along different planes of gliding from those of bischofite.

L. J. S.

Secondary Minerals from Otavi, German S.W. Africa: a New Cadmium Mineral. OTTO SCHNEIDER (*Centr. Min.*, 1906, 388—389).—A preliminary account is given of several minerals from the oxidation-zone of the copper-deposits of Otavi; namely, chessylite (massive and as crystals rich in faces), malachite (fibrous aggregates and pseudomorphs after chessylite), aurichalcite, cerussite (twinned crystals), pyromorphite, linarite, calamine (ZnCO_3), olivenite, greenockite (as a thin, lemon-yellow encrustation on malachite), and a new mineral which is named *otavite*, after the locality. This forms white to red, crystalline crusts lining cavities; it has a strong lustre inclined to metallic-adamantine in character. The minute curved rhombohedra have an angle of about 80° . Analysis shows the mineral to be a basic cadmium carbonate containing 61.5 per cent. of cadmium.

L. J. S.

Argentiferous Lead Mineral from Rosseto, in Elba. NAZARENO TARUGI and A. CALAMAI (*Gazzetta*, 1906, 36, i, 366—369).—On analysis, this mineral gave the following results, expressed in parts per 1000:

Pb.	SiO_2 .	S.	CO_3 (calc.).	Fe_2O_3 .	Ag.	Cu.	CaO, MgO, &c.		
							H_2O .	and loss.	Total.
775	66.6	106	29.151	10.2	1.21	5.889	0.47	5.48	1000

These elements are probably combined as:

PbS.	PbCO_3 .	Ag_2S .	CuS .	SiO_2 .	Fe_2O_3 .	H_2O .	CaO, MgO, &c.		
							and loss.	Total.	
779.03	129.47	1.38	7.37	66.6	10.2	0.47	5.48	1000	

T. H. P.

Scheelite from Traversella. FERRUCCIO ZAMBONINI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 558—565. Compare Colomba, this vol., ii, 369).—The author describes the forms of various scheelite crystals from Traversella, and confirms the statement of Colomba (*loc. cit.*) that the angular deviations found in natural scheelite crystals are independent of the composition.

The best methods of preparing artificial scheelite crystals are those of Drevermann and of Maccé. The habit of the crystals thus obtained depends greatly on the conditions under which they are formed.

T. H. P.

Minerals from the Granite of S. Fedelino (Lake Como). EMILIO REPOSSI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 505—512).—The author describes the characters of specimens of quartz, calcite, titanite, epidote, prehnite, muscovite, chlorite, and laumontite found in the granite of S. Fedelino, in which they occur only rarely.

T. H. P.

Vesuvian Ash of April, 1906. ARRIEN JOHNSEN (*Centr. Min.*, 1906, 385—387).—The grey ash which fell at Naples on April 5, 1906, contains leucite, augite, plagioclase, magnetite, apatite, pale brown glass, and grains consisting of a compact aggregate of minerals. These constituents were separated by means of a heavy liquid, and the calculated chemical composition of the ash corresponds closely with that of Vesuvian ash of 1861, 1872, and 1882, and with a leucite-tephrite lava.

L. J. S.

Sand emitted from Vesuvius. A. OGIALORO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 135—136).—Sand emitted from Vesuvius and collected on April 5th, 8th, 11th, and 13th, 1906, was found to contain appreciable proportions of arsenic in the form of compounds insoluble in ammonia, but soluble in nitric acid. The acidity, which is low, disappears after some time and is probably due to sulphur dioxide. The aqueous extract contains abundant quantities of chlorides, among which are those of ammonium and sodium, marked quantities of sulphates, especially that of calcium, small proportions of potassium compounds, and traces of iron; hydrogen sulphide and phosphates are absent. Phosphates occur copiously in the hydrochloric acid extract, which contains also small quantities of sulphate.

T. H. P.

Volcanic Rocks from Graham's Land, Antarctic. ERNEST GOURDON (*Compt. rend.*, 1906, 143, 178—180).—Petrographical descriptions and chemical analyses are given of trachy-andesites, labradorites and basalts.

L. J. S.

Physiological Chemistry.

Behaviour of an Animal respiring Mixtures of Air and 5 to 10 per cent. of Carbon Dioxide. NESTOR GRÉHANT (*Compt. rend.*, 1906, 143, 104—106).—Experiments with a dog showed that air containing 10 per cent. of carbon dioxide was respired 2·7 times as quickly as pure air. The carbon dioxide in the blood is very slightly increased and the oxygen slightly diminished when the respired air

contains 5 per cent. of carbon dioxide; with 10 per cent. of carbon dioxide, the amount of carbon dioxide was more greatly increased, whilst the oxygen remained constant.

N. H. J. M.

Proteids of Blood Serum. GUSTAVE PATEIN (*J. Pharm. Chim.*, 1906, [vi], 24, 16—21. Compare Abstr., 1899, ii, 827).—The proteids of blood serum are divided into three classes: (1) serum globulin precipitated from dilute solution by acetic acid; (2) serum globulin, non-precipitable by acetic acid; (3) serin. Globulin 1 is estimated by diluting 50 c.c. of serum with 500 c.c. of water, and very carefully adding acetic acid until the solution is distinctly but weakly acid; 2 and 3 together are estimated according to the method already given (*loc. cit.*); the serin is estimated by heat coagulation after separating the globulin 2 by precipitation with magnesium sulphate. The proportions of the three constituents vary for different sera, the sp. gr. of the latter also varying within the range 1·023 to 1·030. Blood serum, which has had its alkalinity neutralised by adding acetic acid, presents well-defined stages of coagulation by heat, the temperatures of coagulation corresponding with those of the so-called euglobulins and pseudo-globulins. A serum having the composition: globulin precipitable by acetic acid, 3·80 grams per litre; globulin non-precipitable, 29·40; serin, 46·20 grams per litre, gave, on heating, 4·20 grams coagulum at 56°, 13·0 grams coagulum at 64—65°, 40·20 grams at 70°, and 22·70 grams at 75—100°.

W. A. D.

Effect of Foods, both Rich and Poor in Fat, in Conjunction with Various Foods, on Milk Secretion. GUSTAV FINGERLING (*Landw. Versuchs-Stat.*, 1906, 64, 299—412. Compare Abstr., 1905, ii, 476).—Replacement of food deficient in fat (barley meal) by one containing more fat (rice meal) increased both the absolute and the percentage amount of fat in milk. By addition of fatty foods, it was found possible to render inferior foods, such as hay which had been exposed to rain, equivalent as regards milk production to normal hay.

The experiments were made with goats.

N. H. J. M.

Elimination of Chloroform by the Urine. MAURICE NICLOUX (*J. Pharm. Chim.*, 1906, [vi], 24, 64—65).—Using the author's method of estimating small quantities of chloroform (this vol., ii, 202), the amount of chloroform in the urine of dogs, subjected for prolonged periods to the anæsthetic, is found to be extremely small, namely, from 6 to 8 milligrams per 100 c.c. of urine.

W. A. D.

Physiological Evidence as to the Constitution of Ammonium Dye Bases. HERMANN FUEHNER (*Ber.*, 1906, 39, 2437—2438).—The typical action of curare is exhibited by those methylated ammonium bases which do not form pseudo-bases, but not by methylated bases of the di- and tri-phenylmethane groups, which, according to Hantzsch, change into pseudo-forms when liberated. An exception to this rule is formed by methylene-blue.

G. Y.

Chemistry of Vegetable Physiology and Agriculture.

Composition of an Acetic Ferment. E. ALLILAIRE (*Compt. rend.*, 1906, 143, 176—178).—The ferment, obtained from a vinegar vat, was centrifugated, washed several times with water, and then macerated with 80 per cent. alcohol for some hours. The dried substance contained 6·9 per cent. of nitrogen and 5·9 per cent. of ash having the following composition :

NaOH.	KOH.	CaO.	MgO.	Fe ₂ O ₃ .	Cu.	H ₃ PO ₄ .	SiO ₂ .
2·87	18·02	10·70	8·00	10·70	1·66	47·45	0·60.

Traces of manganese, sulphur, and chlorine were also present. The substance freed from fat forms a jelly with boiling water.

The alcoholic extract contained a phosphoric fat readily soluble in chloroform. Assuming all the phosphorus to be in the form of lecithin, the fat would contain 50—60 per cent. of this substance.

N. H. J. M.

New Properties of Malt-extract. LÉON MAQUENNE and EUGÈNE ROUX (*Compt. rend.*, 1906, 142, 1387—1392).—The activity of malt-extract, when prepared quickly, increases with rest owing to an auto-excitation. The alkaline reaction, termed the optimum from the double point of view of the rate of saccharification and the amount of maltose produced, is the same for fresh malts and for such as are already excited or weakened. The normal saccharification of starch takes place as if the amylo-pectin were only attacked by a diastase secreted in the course of the auto-excitation of the malt. The transformation of pure amylose into maltose is extremely rapid, and the residual dextrins of ordinary saccharification seem to be derived exclusively from the amylo-pectin already liquefied but not yet saccharified.

N. H. J. M.

Transformation of Cinnamic Acid into Styrene by Moulds. OLIVIERO (*J. Pharm. Chim.*, 1906, [vi], 24, 62—64).—An aqueous extract of *Aspergillus niger* or *Penicillium glaucum*, filtered through a Chamberland filter, rapidly decomposes sodium cinnamate dissolved in water, giving styrene; the action is due to an enzyme secreted by the mould, and may be used as a test for the presence of *Aspergillus* or *Penicillium*, the styrene being at once recognised by its odour.

W. A. D.

Pro-invertase and Reversibility of the Invertase in Mucor. ENRICO PANTANELLI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 587—594).—The cells of *Mucor stolonifer* and *Mucor mucedo* contain a pro-invertase or zymogen of invertase, which is secreted as such and is then slowly transformed into active invertase in the external liquid. This transformation is possibly due to a slow oxidation; indeed, aëration facilitates the change, although it is accomplished in the absence of free oxygen. The change of pro-enzyme into enzyme is

catalysed by hydrogen ions, which are, in fact, necessary to it, although in minute quantities; the rate of the change varies proportionally with the affinity constant of the acid employed.

In a neutral or even a faintly alkaline medium, the active enzyme becomes destroyed more rapidly than in an acid medium, whilst the pro-invertase keeps for a long time, even in an alkaline medium. Indeed, if an alkaline mash of the mould, which is rapidly losing its inverting capacity, is faintly acidified after a few days, its power to invert is gradually restored.

The passage from the secreted pro-invertase into invertase is similar to that taking place with intracellular zymogen, but the optimum acidity for the change is higher in the former than in the latter case.

In a faintly alkaline liquid, invertase is capable of a very considerable reversionary action, the amount of the reversion varying inversely with the acidity, and in alkaline media proportionally to the concentration of hydroxyl ions, provided that this does not exceed a certain limit.

In one of the author's experiments on the action of invertase on an alkaline solution of invert sugar, as much as 24 per cent. of the original hexose underwent reversion after being maintained at 18.5° for twenty-four hours.

T. H. P.

Influence of the Absorption of Sugars on Germination. W. LUBIMENKO (*Compt. rend.*, 1906, 143, 130—133).—When fermentable sugars are absorbed by the higher plants, the latter induce alcoholic fermentation of the sugars even in presence of oxygen. Higher plants behave, therefore, like yeasts under aerobic conditions.

N. H. J. M.

Spectroscopic Study of the Green Pigments of Ripe Seeds. W. LUBIMENKO (*Compt. rend.*, 1906, 142, 1432—1435).—The green pigments differ from chlorophyll, but it is uncertain whether they consist of chlorophyll which has been altered or whether they are intermediate products of chlorophyll.

N. H. J. M.

Possibility of accumulating Arsenic in the Fruits of Certain Plants. B. GOSIO (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 730—731).—The author's experiments were made with *Cucurbita pepo*, which was sheltered from the rain and watered first with water, later with a solution of 1 part of sodium arsenite in 100,000 of water, and finally with a solution of 1 part of the same salt in 10,000 of water. It is found that, in these circumstances, the fruit accumulates arsenic until it contains as much as 0.0041 per cent. of this element.

T. H. P.

Chemical Composition of Chestnut Flour, and Study of Two Sugars contained therein. RAFFAELE PALADINO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 117—123).—The following results were obtained on analysis of flour from the fruit of *Castanea vesca*: water, 10 per cent.; acidity, 0.009 per cent., calculated as sulphuric acid; ash, 2.20 per cent., containing 9.44 per cent. of P_2O_5 , besides

carbonates, chlorides, and sulphates; the ethereal extract of the flour contains 3.84 per cent. of P_2O_5 ; fatty substances and castanosterol, 2.87 per cent.; nitrogen, 1.96 per cent., corresponding with 12.25 per cent. of proteid substances; dextrin, 9.22 per cent.; cellulose, 4.8 per cent.; soluble substances, 29.30, and reducing sugars 13.10 per cent.

Two sugars were detected: (1) one from the alcoholic extract of the flour, melting at 160° and giving crystals resembling those of sucrose; it reduces only after hydrolysis, is not fermented by beer yeast, gives an osazone melting at 204° , and has a specific rotation corresponding with that of sucrose; (2) the aqueous extract yields a reducing, syrupy, dextrorotatory sugar, which is fermented by beer yeast and gives an osazone melting at 204° .

T. H. P.

The Alkaloids of Coca. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1906, 25, 233—237. Compare this vol., ii, 315).—The quantity of alkaloids in the leaves of the coca plant decreases with the age of the leaf for plants of the same age, being 4.70 per cent. of the dried material in the case of the partially-developed leaves near the growing point, and 1.22 per cent. in the fully-developed leaves; this diminution is due to the increase in the leaf and not to any loss of alkaloid, for if the quantity of alkaloid in each leaf is calculated as a percentage of the mean weight of a fully-developed leaf, the numbers thus obtained are practically constant. The quantity of alkaloids in leaves of the same age of different plants is independent of the age of the plant.

The nature of the alkaloids varies with the age of the leaf, and, owing to a transformation of the cinnamylcocaine into cocaine or δ -isatropylcocaine, the amount of cinnamylcocaine in the alkaloids extracted from the young and old leaves is 61.5 to 62.7 per cent. and 21.3 to 25.8 per cent. respectively, the corresponding values for cocaine being 33.5 to 34.3 per cent. and 71.3 to 74.4 per cent.

M. A. W.

Grapes from the Region of Schariare, Persia. OCTAVE LECOMTE (*J. Pharm. Chim.*, 1906, [vi], 24, 24—25).—Analyses are given of the juice of grapes from different localities in the district. The juice is in all cases very rich in fermentable sugar, and should therefore give strongly alcoholic wines. The presence of sucrose was established in the case of one of the white grapes.

W. A. D.

Cyanogenetic Principles of Phaseolus lunatus. ÉMILE KOHN-ABREST (*Compt. rend.*, 1906, 143, 182—184).—Numerous cyanogenetic glucosides occur in the mixtures termed Java peas: no doubt as many as there are of varieties of *Phaseolus lunatus*.

N. H. J. M.

Lupins. HUGO NEUBAUER (*Landw. Versuchs-Stat.*, 1906, 64, 253—297).—The botanical characteristics, chemical composition, and food value of lupins are discussed.

N. H. J. M.

Microbiology of Soils. BERTHOLD HEINZE (*Centr. Bakt. Par.*, 1906, 16, ii, 640—653 and 703—771).—The considerable importance of algæ in fixation of nitrogen in soils is attributed to the fact that they furnish nitrogen-fixing microbes, especially *Azotobacter*, with

suitable carbonaceous food (mannitol, glycogen, pentosans, pentoses, &c.). It is therefore wrong to assume, as Gautier and Drouin have done, that their only importance consists in preventing losses of ammonia in the soil.

N. H. J. M.

Phospho-humic Compounds of the Soil. J. DUMONT (*Compt. rend.*, 1906, **143**, 186—189. Compare Abstr., 1905, ii, 196).—A solution of potassium humate when treated with phosphoric acid absorbed 6.1 per cent. With monocalcium phosphate an abundant precipitate was formed, and a still greater amount of phosphoric acid was absorbed. Humus precipitated, in presence of dipotassium phosphate, by acetic, citric, hydrochloric, and sulphuric acids was found to contain about the same amounts of phosphoric acid. The amount of phosphoric acid taken up was not affected to any extent by differences in the amount of phosphate added.

N. H. J. M.

Analytical Chemistry.

New Method of Estimating Moisture, with Special Application to Moisture in Cordite and other Substances containing Volatile Matters other than Water. P. V. DUPRÉ (*Analyst*, 1906, 31, 213—217)—A weighed quantity of the substance in which the moisture is to be estimated is placed in a tube about 1 cm. in diameter and 12 cm. in length, and is then covered with a thin layer of sand, calcium carbide being now filled in to a depth of about 5 cm. The tube is connected with a nitrometer containing saturated sodium chloride solution, and after adjusting the level of this solution and the temperature of the tube, the latter is immersed to a depth of 8 cm. in a boiling water-bath, the heating being continued until no further evolution of gas can be observed. The tube is then cooled to the original temperature and the volume of the acetylene read off. As the average of a number of experiments, 1 c.c. of acetylene at N.T.P. was found to be equivalent to 0.001725 gram of water. The theoretical figure should be 0.00162, but the calcium hydroxide formed retains a small quantity of water, which quantity, however, is always proportional to the amount of acetylene produced. The method is applicable to the estimation of water in crystallised salts, and moisture in cordite, in explosives containing ammonium oxalate or magnesium sulphate, and in mixtures containing a volatile constituent, such as naphthalene or camphor. In the case of explosives containing ammonium oxalate, &c., the quantity of the salt present must be estimated separately in order to obtain the amount of water present as moisture. Experiments are also given to show that the combined water in salts may be distinguished from any water present in the uncombined state. The combined water commences to be lost at once

on applying the heat, and the loss continues during the whole period taken for the uncombined water to be driven off. This loss appears to take place at one-half the rate of the loss of the combined water after all the uncombined water has disappeared. W. P. S.

Behaviour of Ozone with Tetramethyldi-*p*-diaminodiphenylmethane. FRANZ FISCHER and HANS MARX (*Ber.*, 1906, 39, 2555—2557. Compare Arnold, *Abstr.*, 1902, ii, 352, 691; this vol., ii, 390).—Wet "tetramethyl-base paper" is coloured violet by ozone and yellow by nitric oxide, whereas a mixture of the gases produces a dirty-brown coloration. The violet colour produced by ozone is converted into yellow by prolonged exposure to nitric oxide, and *vice versa*. To detect a minute quantity of nitric oxide in ozone, the mixture must be led into liquid air, whereby the ozone is dissolved and the nitric oxide solidified. After filtration the two substances can be identified.

Dry "tetramethyl-base paper" develops a yellow coloration with ozone. C. S.

Rapid and Exact Method of Estimating Sulphates and Barium Salts. NAZARENO TARUGI and G. BIANCHI (*Gazzetta*, 1906, 36, i, 347—358).—This method is based on the observation that if a sulphate is precipitated by means of barium chloride and some of the turbid liquid forced up a narrow tube, the clarification of the liquid is almost instantaneous, so that it can be ascertained immediately whether the addition of more barium chloride causes any further turbidity.

A convenient form of apparatus in which to carry out the estimation consists of a flask of about 300 c.c. capacity fitted with a three-holed stopper through which pass: (1) a short tube bent in a U-shape, and containing a little mercury to act as a manometer; (2) a narrow tube reaching to within about 2 cm. of the bottom of the flask, and connected at the top with rubber tubing to a small funnel, the stem of which has as nearly as possible the same bore and thickness of walls as the tube; the rubber connection is fitted with a pinch-cock; (3) a short tube in which is inserted a stop-cock.

An aliquot portion of the sulphate solution to be examined, acidified with nitric or hydrochloric acid, is introduced into the flask, the stopper inserted, and about the right volume of standard barium chloride solution run from a burette into the funnel, and thence washed down into the flask and well mixed with the sulphate solution by bubbling air through the liquid. The flask is then heated in a calcium chloride bath, and when the temperature reaches 60—70° the funnel pinch-cock and the stop-cock are closed. In this way pressure is developed in the flask, and when the mercury manometer indicates that this has reached a sufficiently high value the pinch-cock is gradually opened until the liquid rises in the tube nearly to the rubber connection, when the cock is again closed. In a few minutes the upper portion of the liquid thus drawn up becomes clear, and when this is the case the pinch-cock is again opened to allow of 2 or 3 c.c. of this liquid entering the funnel. It is here tested by adding a drop of the standard barium chloride solution. If this produces a turbidity, a further quantity of

the barium chloride solution is washed down into the flask, mixed with the liquid, and the process repeated. In this way two volumes of the barium chloride solution are obtained, one just producing and the other just not producing turbidity in the solution. The mean of these volumes, which differ but slightly, is taken as the amount required to precipitate the sulphate present. If too much of the barium chloride solution is added, standard sulphuric acid solution may be added.

It is advisable to make several separate estimations which can all be carried out in about an hour, and take the mean of the results obtained. The results arrived at in this way agree extremely closely with those obtained by weighing the barium sulphate.

Barium salts are, of course, determined by means of standard sulphuric acid solution, the procedure being the same as that described above.

T. H. P.

The Nitrometer. J. NEWFIELD and J. P. MARX (*J. Amer. Chem. Soc.*, 1906, **28**, 877—882).—The Lunge nitrometer (gas volumeter) is recommended for estimating the nitric nitrogen in gun-cotton and other explosives.

The results, however, are much affected by the strength of the sulphuric acid used, temperature, pressure, time of action, and presence of other organic substances. For further particulars as to the best method of using the nitrometer, the original paper should be consulted.

L. DE K.

Estimation of Certain Oxidising Substances by means of Hydrazine Sulphate. L. MEDRI (*Gazzetta*, 1906, **36**, i, 373—378).—According to Roberto and Roncali (*Abstr.*, 1904, ii, 773), when hydrazine sulphate is gently heated with potassium permanganate, nitrogen is evolved according to the equations $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 5\text{O} + 3\text{H}_2\text{O}$ and $5\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4 + 5\text{O}_2 = 10\text{H}_2\text{O} + 5\text{H}_2\text{SO}_4 + 5\text{N}_2$.

The author finds, however, that the reaction never proceeds according to these equations, which are also not in accord with the results of Petersen (*Abstr.*, 1893, ii, 605).

The results of the author's experiments show that in the action of potassium permanganate solution on excess of hydrazine sulphate solution acidified with sulphuric acid the hydrazine is not completely oxidised, but nitrogen is evolved in agreement with the equation given by Petersen (*loc. cit.*): $17\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4 + 13\text{O} = 13\text{H}_2\text{O} + 7(\text{NH}_4)_2\text{SO}_4 + 10\text{N}_2 + 10\text{H}_2\text{SO}_4$.

The amount of sulphuric acid present may vary between wide limits without sensibly influencing the exactness of the results, but the presence of the acid is necessary for the reaction to proceed. In absence of sulphuric acid, the degree of oxidation of the hydrazine salt rises, but never to the extent required by the equations of Roberto and Roncali.

Hence the estimation of hydrazine by measuring the volume of nitrogen evolved in its action on permanganate leads to erroneous results, because the sulphuric acid required can, after the oxidation of the hydrazine, act on the permanganate and cause oxygen to be

evolved. When, however, it is a question of estimating permanganate by means of hydrazine, the acid is prevented from acting on the permanganate by the constant presence of excess of the reducing agent.

Hydrazine is, however, completely oxidised by potassium dichromate (see Purgotti, *Abstr.*, 1897, ii, 349). T. H. P.

The Gutzeit Test for Arsenic. J. ARCHIBALD GOODE and F. MOLLWO PERKIN (*J. Soc. Chem. Ind.*, 1906, 25, 507—510).—The authors prefer to use magnesium and ammonium chloride solution for evolving the hydrogen in this test. The evolution flask should have a capacity of about 250 c.c., and the hydrogen must be passed through a 10 per cent. solution of acid cuprous chloride contained in a U-tube attached to the delivery tube of the flask. This solution absorbs any hydrogen sulphide which may be present. The mercury paper is fixed over the other end of the U-tube. Paper soaked in an alcoholic mercuric bromide solution is stated to be rather more sensitive than mercuric chloride paper. Unsuccessful attempts were made to obtain permanent standard colorations by the use of paper soaked in gold chloride solution. If phosphorus compounds are present in the substance tested, they must be oxidised with bromine before applying the test. W. P. S.

Estimation of Minute Quantities of Arsenic in Organic Substances. NAZARENO TARUGI and A. BIGAZZI (*Gazzetta*, 1906, 36, i, 359—364. Compare *Abstr.*, 1903, ii, 240).—In part polemical. When the organic matter is destroyed by Gautier's method (*Abstr.*, 1903, ii, 612), the whole of the arsenic never passes into the aqueous solution. T. H. P.

Detection and Estimation of Boric Acid [in Foods]. WILSON H. LOW (*J. Amer. Chem. Soc.*, 1906, 28, 807—823).—*New Application of the Turmeric Test.*—Ten grams of the sample (hashed meat, for instance) are mixed with 5 c.c. of *N*/2 solution of sodium carbonate, dried, and heated until volatile matter is completely driven off. The charred mass is powdered and treated with 10 c.c. of water and 1 c.c. of strong hydrochloric acid. After testing a small portion of the filtrate as usual, the remainder is placed in a shallow dish with a piece of turmeric paper and allowed to evaporate at 40—50° in a desiccator, if necessary in a vacuum. This test is much more delicate than drying on a steam-bath.

Estimation of Boric Acid.—The charred mass is treated with hydrochloric acid, a little solid calcium chloride is added, and the whole is distilled in a current of methyl alcohol until the distillate no longer contains boric acid. If calcium chloride is not added, a considerable amount of boric acid will be retained in the distilling flask. The distillate is first neutralised with *N*-sodium hydroxide, using *p*-nitrophenol as indicator; more alkali is then added with phenolphthalein as indicator, the methyl alcohol is completely expelled, and the residue is now treated as usual by the well-known glycerol method. L. DE K.

Volumetric Estimation of Carbon in Iron and Steel with the Use of Barium Hydroxide. JAMES A. AUPPERLE (*J. Amer. Chem. Soc.*, 1906, 28, 858—862).—The sample is burnt in a current of air or oxygen in an Aupperle crucible, and the resulting carbon dioxide is absorbed in standardised barium hydroxide solution. The free alkali is then at once titrated with standard hydrochloric acid without removing the precipitated barium carbonate. L. DE K.

Estimation of Carbon in Iron and Steel by Direct Combustion with Red Lead. CHARLES M. JOHNSON (*J. Amer. Chem. Soc.*, 1906, 28, 862—877).—The process, which is applicable to all kinds of iron and steel, consists in burning the sample in presence of red lead in a current of purified oxygen. The use of copper oxide in the combustion is unnecessary. For details and description of absorbing apparatus, the original article should be consulted. L. DE K.

Scheibler's Apparatus for the Estimation of Carbon Dioxide in Carbonates; an Improved Construction and Use for Accurate Analysis. S. HOARE COLLINS (*J. Soc. Chem. Ind.*, 1906, 25, 518—522).—In the modification of Scheibler's apparatus which is described, a small bulb is placed above the decomposition flask to prevent the acid from splashing up into the rubber tubes. This bulb, together with the rubber connecting tube, has a capacity of about 15 c.c. If 15 c.c. of gas pass into the burette, no carbon dioxide passes into the burette at all; the error due to absorption is therefore nil. If 30 c.c. of gas pass into the burette there will be only 8.8 per cent. of carbon dioxide in the latter. Gas of such concentration would need 3.4 c.c. of water to be saturated before 0.3 c.c. had been absorbed; hence an error of 1 per cent. is impossible. The whole of the apparatus described is enclosed in a large vessel containing water, the latter being mixed by a current of air blown through it by means of a bellows arrangement, the latter also serving to adjust the level of the water in the burette to the zero point. The author also discusses the errors in Scheibler's method due to temperature, solubility of carbon dioxide in water and acids, the disturbing influence of various salts, alteration of volume by bending the rubber connections, and occluded gas in the substance analysed. W. P. S.

Estimation of Silica in Iron Ores containing Alumina. GRAHAM DEAN (*J. Amer. Chem. Soc.*, 1906, 28, 882—883).—One gram of the ore is boiled with 25 c.c. of hydrochloric acid, and when all is dissolved a few drops of nitric acid are added and the whole is evaporated to dryness. The residue is boiled with hydrochloric acid, slightly diluted with water, and the undissolved portion is collected on a filter and washed with hot acid (1:1). It is then transferred to a platinum crucible and ignited for a few minutes. When cold, the residue is transferred to a beaker and boiled for eight minutes with strong hydrochloric acid. The insoluble matter, which may now be regarded as practically pure silica, is collected and weighed as usual; the filtrate is united with the first, main, filtrate.

For the precipitation of the alumina, the phenylhydrazine process is recommended. L. DE K.

Estimation of Potassium by means of Chloroplatinic Acid in Presence of Sulphates. KARL REGEL (*Chem. Zeit.*, 1906, 30, 684—685).—The author works according to Fresenius's directions, but does not remove any sulphates, and the potassium platinichloride obtained may therefore contain an admixture of sodium or even calcium sulphate. The precipitate is now dissolved in boiling water and treated with a slight excess of powdered magnesium. The platinum separates as metal, which is then freed from the adhering salts and the excess of magnesium by washing with dilute hydrochloric acid. The metal is at once ignited and weighed.

In presence of calcium sulphate, the mass is washed first with water and then with 5 per cent. nitric acid.

L. DE K.

Estimation of Sodium Chloride in Yolk of Egg. L. GADAIS and J. GADAIS (*Ann. Chim. anal.*, 1906, 11, 249).—One gram of the sample is mixed in a crucible with 12 grams of pure potassium nitrate and two drops of aqueous sodium hydroxide, and heated very gradually until finally a clear, fused mass is obtained. When cold, the mass is dissolved in water and neutralised with pure nitric acid, any accidental excess of which is neutralised with calcium carbonate. The salt is then estimated in the usual way with $N/10$ silver nitrate, with potassium chromate as indicator. The presence of borates does not interfere.

L. DE K.

Estimation of Small Quantities of Manganese. New Method of Formation of Glycerose. NAZARENO TARUGI (*Gazzetta*, 1906, 36, i, 332—347).—The method here described for estimating small quantities of manganese is based on the solubility of manganous hydroxide in glycerol and on the readiness with which such a solution oxidises, by the action either of the air or of sodium hypochlorite; this oxidation is accompanied by the production of a ruby-red colour, the intensity of which is exactly proportional to the quantity of manganese present.

It is of no consequence in what proportions the reagents and solution are used, but the conditions must be identical in the actual test and in the parallel experiment made at the same time with a known amount of manganese. It is convenient to use a check solution containing 0.316 per cent. of potassium permanganate, this corresponding with 0.11 per cent. of manganese. The estimation may be carried out as follows: to 5 c.c. of the manganese solution are added 3 c.c. of glycerol and then 1 c.c. of about 50 per cent. sodium hydroxide solution; a slow current of air (twenty minutes) or oxygen (ten minutes) is then passed through the cold solution. The air or oxygen may be replaced by 10 c.c. of a solution of sodium hypochlorite containing 3 per cent. of active chlorine, but the use of this reagent is inadmissible in certain cases, specified below. The addition of alkali may cause the precipitation of insoluble hydroxides, but when these settle the estimation may be made in the usual way. If the solution to be examined and the standard permanganate solution give colours differing in intensity, one of the liquids must be diluted so as to render the tints identical. Two tubes of equal diameter may be conveniently employed.

Salts of copper or cobalt exert practically no influence on the colour

when their concentration is less than 0.1 per cent. If a higher proportion of copper is present, it may be removed by the action of metallic iron, the solution being subsequently reoxidised by means of nitric acid. If it is necessary to remove chromium or cobalt or both of these metals, and at the same time copper, the liquid is heated with ammonia and ammonium persulphate; the precipitated manganese is collected on a filter, washed, and dissolved in hydrochloric acid.

This method is capable of estimating 0.00001 gram of manganese with moderate exactness. By placing a drop of the manganese solution on a white tile and adding first a drop of glycerol and then a drop of soda solution and allowing the mixture to stand for a few minutes in the air, estimation of quantities of manganese as small as 0.0000005 gram can be roughly made.

Sodium hypochlorite has an extremely slow action on glycerol, but the presence of a very small quantity of a cobalt salt (1 drop of a 0.1 per cent. solution) renders the action very vigorous. In this reaction glycerose is formed, and in one experiment 18 per cent. of the glycerol present was converted into the sugar. T. H. P.

Analysis of Platinum Metals. N. A. ORLOFF (*Chem. Zeit.*, 1906, 30, 714—715).—Osmium may be separated from the other platinum metals by precipitating the solution with zinc or magnesium and then treating the deposit with hydrogen peroxide. The osmium dissolves as tetroxide, whilst the other metals are not affected. It may be recovered from the solution in the usual manner.

Palladium may be separated from the other members of the group by treating the solution with freshly-precipitated silver iodide, which precipitates the palladium as iodide. The metal may be extracted from the precipitate by means of potassium thiocyanate, also by heating and subsequent extraction with nitro-hydrochloric acid. L. DE K.

Determination of the Hardness of Waters. GAETANO MAGNANINI (*Gazzetta*, 1906, 36, i, 369—373).—It has been stated that in determining the hardness of water by means of standard soap solution, the presence of small quantities of magnesia influences the accuracy of the results. The author has added varying amounts of lime, baryta, and magnesia to water and has then determined the hardness by means of soap solution in two different ways: (1) by shaking the liquid immediately after the addition of the soap solution; (2) by allowing a few minutes to elapse after each addition of soap solution and before shaking. It is found that, with waters containing either lime or baryta or the two together, the same results are obtained by the two methods of working. When magnesia is present, however, the second method alone gives accurate and concordant results. The reason of this is that the magnesia reacts slowly with the soap, and only when time is allowed for this to take place can a permanent lather be obtained. T. H. P.

Use of Copper Oxide in Elementary Analysis. MAX DENNSTEDT (*J. pr. Chem.*, 1906, [ii], 73, 570—574. Compare this vol., ii, 51, 306, 398; Dennstedt and Hassler, *Abstr.*, 1903, ii, 686).—A criticism of Marek's suggestions (this vol., ii, 496). The use of a roll

of oxidised copper gauze instead of a layer of platinum would entail all the disadvantages of the ordinary methods of combustion.

G. Y.

Modification of Liebig's Potash Bulbs. R. VILLIERS (*Ann. Chim. anal.*, 1906, 11, 250).—The apparatus differs from the original design in so far that the centres of the bulbs are no longer on a horizontal line. The volume of liquid introduced must be such that when the gases traverse the apparatus the inlet and exit tubes take the horizontal position. The smaller bulbs still retain a sufficiently oblique position to cause an effective absorption of the gas. L. DE K.

Preparation and Distinctive Properties of Empyreumatic Oil of Juniper (*Oleum cadi*). CAMILLE PÉPIN (*J. Pharm. Chim.*, 1906, [vi], 24, 49—58. Compare Troeger and Feldmann, *Abstr.*, 1899, i, 376; Cathelineau and Hausser, *Abstr.*, 1899, i, 536, 711; 1900, i, 510; 1901, i, 283; 1902, i, 44).—The origin of *Oleum cadi* has hitherto been uncertain, and all earlier experiments have been made with material of doubtful genuineness. The true *Oleum cadi* is made in the departments of Var and Gard by the dry distillation of the wood of *Juniperus oxycedrus*. It is often adulterated by the addition of pine-wood tar; this substance can be detected by the light petroleum extract of the oil assuming a green coloration with copper acetate under certain conditions. The pure oil from *Juniperus oxycedrus* does not respond to this test, but an oil prepared from this wood mixed with that of other species of *Juniperus* behaves like the oil containing pine tar. W. A. D.

Direct Estimation of Nitroglycerol in Cordite, &c. OSWALD SILBERRAD, HENRY A. PHILLIPS, and HENRY J. MERRIMAN (*J. Soc. Chem. Ind.*, 1906, 25, 628—630).—The direct estimation of nitroglycerol in a cordite is carried out as follows: a weighed quantity of the ground cordite, sufficient to yield about two grams of nitroglycerol, is extracted thoroughly in a Soxhlet apparatus with 80 c.c. of absolute ether. When the extraction is complete, the residual nitrocellulose is removed from the extractor and two absorption flasks containing 10 c.c. of *N*/10 acid are connected to the top of the condenser. Fifty c.c. of a 5 per cent. alcoholic sodium ethoxide solution are added to the extraction flask through a small side tube and the heating on the water-bath continued for about six hours. The ether is then distilled up into the Soxhlet apparatus and run off by means of a tapped tube; the residue is dissolved in water and made up to a volume of 250 c.c., the aqueous Soxhlet and ether washings being also added to the solution. Fifty c.c. of the solution are now placed in a flask, 50 grams of a mixture of powdered zinc (2 parts) and reduced iron (1 part) are added, together with 50 c.c. of a 40 per cent. sodium hydroxide solution, and the ammonia distilled off in a slow current of air. The ammonia is collected in a known volume of *N*/10 acid contained in an absorption flask and the excess of the acid is titrated at the end of the distillation. One c.c. of *N*/10 acid corresponds with 0.00757 gram of nitroglycerol.

W. P. S.

Source of Error in Sugar Analyses owing to Formation of Ethers of Dextrose. Mlle. TALON (*Ann. Chim. anal.*, 1906, 11, 244—245).—In presence of ethyl or methyl alcohol, the acid inversion process of sugar yields ethers of dextrose which seriously affect the accuracy of the results obtained polarimetrically or by titration. Any alcohol present should, therefore, first be got rid of by evaporation.

Small quantities of glycerol do not interfere with the estimation.

L. DE K.

Reducing Sugar Methods. LEWIS S. MUNSON and PERCY H. WALKER (*J. Amer. Chem. Soc.*, 1906, 28, 663—686).—The authors have constructed a lengthy table for the benefit of those engaged in gravimetric sugar analyses. The table runs from 10 to 490 milligrams of cuprous oxide (8.9 to 435.3 milligrams of metallic copper) and contains the corresponding amounts of dextrose, invert sugar, and invert sugar when accompanied by sucrose in small and in large proportion.

When using this table it is necessary to follow the same *modus operandi* as used by the authors. This consists in introducing 50 c.c. of Fehling-Soxhlet copper solution into a flask and adding 50 c.c. of sugar solution containing not more than about 0.23 gram of reducing sugar. The whole is then heated to boiling and kept so for exactly two minutes. The cuprous oxide is collected on a weighed asbestos filter placed in a Gooch crucible, washed first with hot water, then with alcohol, and finally with ether. It is then dried at 100° and weighed.

It is advisable to make an experiment without addition of sugar and allow for any precipitate thus obtained.

L. DE K.

Volumetric Estimation of Formaldehyde and of Formic Acid with Potassium Permanganate in Acid Solution. HERMANN GROSSMANN and ARTHUR AUFRECHT (*Ber.*, 1906, 39, 2455—2458).—Vanino and Seitter's method for the estimation of formaldehyde (*Abstr.*, 1902, ii, 55) leads to consistent results if the reaction is allowed to proceed for at least one hour.

The estimation of formic acid or of a formate is carried out thus: 50 c.c. of the solution of formic acid (0.18 per cent.), 50 c.c. of *N*/10 permanganate, and 200 c.c. of 20 per cent. sulphuric acid in a stoppered vessel are kept for about six hours at the ordinary temperature or four and a half hours on the water-bath; the oxide of manganese and excess of permanganate are destroyed by a small excess of standard oxalic acid at 40°, and the solution is finally titrated with standard permanganate. A blank experiment must be performed simultaneously.

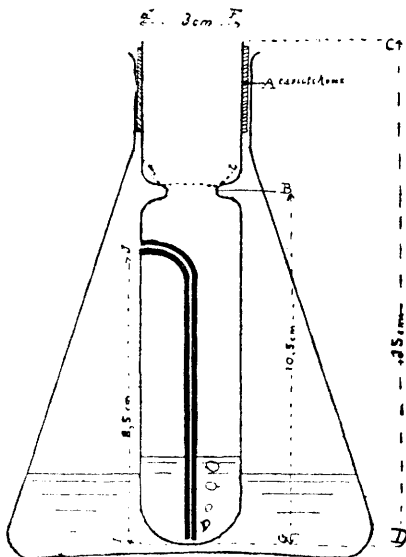
C. S.

The "Aldehyde Figure" of Milk. H. DROOP RICHMOND and F. H. MILLER (*Analyst*, 1906, 31, 224—226).—The results of the authors' experiments with Steinegger's process (this vol., ii, 130) show that milk contains both aromatic and fatty amino-groups which condense with formaldehyde, but that the "aldehyde figure" is not a complete measure of the amino-groups or of the formaldehyde condensed. The "aldehyde figure" measures the difference between the points of neutrality of the two reversible reactions: $\text{NH}_2\cdot\text{R}\cdot\text{CO}_2\text{H} + \text{NaOH} \rightleftharpoons \text{NH}_2\cdot\text{R}\cdot\text{CO}_2\text{Na} + \text{H}_2\text{O}$ and $\text{CH}_2\cdot\text{N}\cdot\text{R}\cdot\text{CO}_2\text{H} + \text{NaOH} \rightleftharpoons \text{CH}_2\cdot\text{N}\cdot\text{R}\cdot\text{CO}_2\text{Na}$

+ H_2O . All alkalis do not give the same "aldehyde figure"; with strontium hydroxide solution the results are 1.1 times higher than with sodium hydroxide solution, and the former is to be preferred as it gives a somewhat sharper titration. The mean of 113 estimations gave 19.9 c.c. $N/1$ strontium hydroxide per litre of milk as the mean "aldehyde figure," with 22.6 c.c. as a maximum and 18.1 c.c. as a minimum.

W. P. S.

Estimation of Volatile Acidity in Wines. A. HUBERT (*Ann. Chim. anal.*, 1906, 11, 245—248).—One hundred c.c. of water are introduced into the flask, which should be made of Jena glass, and this is then closed by the tube furnished with a caoutchouc ring (A); 5 or 10 c.c. of the wine are introduced into the tube and into the narrow part (B) is placed a disc of silver or platinum wire gauze. After boiling vigorously for thirty-five minutes, all volatile free acid is expelled, and, on cooling, the wine finds its way into the flask owing to the vacuum produced. A little water is squirted into the tube three or four times, and it is finally lifted out and rinsed once more. The liquid is then titrated and the difference between the result and the total acidity represents the volatile free acidity.



If it is desired to know the total volatile acidity, 25 c.c. of wine should be mixed with 2 or 3 c.c. of syrupy phosphoric acid before going through the process.

L. DE K.

Estimation of Malic Acid and some Fixed Acids in the Juices of Fruits, both Fermented and Unfermented. W. MESTREZAT (*Compt. rend.*, 1906, 143, 185—186).—The juice is neutralised with barium hydroxide, acidified with 3—4 drops of 3 per cent. acetic acid, and concentrated in a vacuum to a volume of 15 c.c. Two c.c. of 30 per cent. barium acetate and then alcohol are added, and the whole filtered. The precipitate is treated with water containing enough sulphuric acid to liberate the organic acids and diluted to 100 c.c. with strong alcohol, which precipitates gums, pectin substances, and proteids. In one portion of the filtered solution, tartaric acid is separated by means of potassium chloride and acetate. The solution containing malic and succinic acids and tannins is then neutralised with barium hydroxide and acidified as before with acetic acid and precipitated with alcohol. The precipitate is redissolved

in water with a little hydrochloric acid and the tannin precipitated with Laborde's aceto-mercuric solution. The malic acid is then determined by titration with $N/5$ permanganate and sulphuric acid. The dried solution extracted with ether yields pure succinic acid.

N. H. J. M.

Differentiation of the Two Pharmaceutical Benzoic Acids. H. CORMIMBŒUF and L. GROSAN (*Ann. Chim. anal.*, 1906, 11, 243—244).—The authors give a test for distinguishing synthetic benzoic acid made from toluene from the natural acid made from benzoin. The latter gives a pleasant aromatic odour when heated with a solution of sodium carbonate, but this test may be defeated easily by adding a suitable aroma to the artificial product. The new test is based on the fact that the synthetic product, owing to its method of preparation, always contains organic chlorine. This may be detected by igniting the sample with its own weight of sodium carbonate and testing for chlorine in the ash.

L. DE K.

Index of Oxidation of Milk. EZIO COMANDUCCI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 113—115).—The author finds that the volume of $N/10$ permanganate solution required to oxidise, in presence of sulphuric acid, a given quantity of genuine milk is practically constant for the milk of any particular animal. He suggests the determination of this constant as a means of ascertaining whether water has been added to, or cream removed from, milk. The determination is carried out as follows: 10 c.c. of a solution prepared by making 10 c.c. of the milk up to 1 litre with distilled water are mixed with 20 c.c. of dilute sulphuric acid (1:5) and the mixture heated at 60—70° on a water-bath, $N/10$ potassium permanganate solution being added drop by drop during the heating until the red colour of the permanganate persists for at least five minutes. Proceeding in this way, the author finds that the number of c.c. of the permanganate required to oxidise 1 c.c. of the milk, which number he terms the "index of oxidation of the milk," varies for the milks of different animals between the following limits: cow, 50—52; goat, 44—46; sheep, 43—48; ass, 55—58; and woman, 53—60. The index diminishes in proportion to the amount of water added, so that cow's milk containing 50 per cent. of water gives an index of 25. Cow's milk from which all the cream has been removed yields a value of 40—42.

T. H. P.

Analysis of Dried Milk. H. DROOP RICHMOND (*Analyst*, 1906, 31, 219—222).—The methods employed for the analysis of ordinary milk require a few slight modifications before they can be applied to dried milk. The fat is best estimated by the Werner-Schmidt method; if there is no other sugar than lactose present, the fat, after drying, should be dissolved in light petroleum and any insoluble residue subtracted from the total weight. In cases where other sugars are present, the ethereal solution of the fat should be mixed with an equal volume of light petroleum and shaken with water rendered slightly ammoniacal, before the solution is evaporated. The milk lactose may

be estimated polarimetrically and the proteids calculated by multiplying the total nitrogen, by Kjeldahl's method, by 6.87. The ash, lime, and phosphoric acid are estimated in the usual way. From the results of seven analyses given, it appears that the lactose in dried milk is present partly in the anhydrous and partly in the hydrated condition. Two of the samples apparently contained calcium saccharate and one of them contained added phosphate. Sucrose was present, as such, in two of the samples.

W. P. S.

Extraction of Fat from Fæces; Occurrence of Lecithin.

JOHN H. LONG (*J. Amer. Chem. Soc.*, 1906, 28, 704—706).—The sample, which should be slightly acidified with hydrochloric acid so as to decompose any soapy matter, is treated in the same manner as milk by the paper coil (Adams's) method. The results are slightly in excess of those obtained by the sand method, but the author considers them more trustworthy.

In the crude fat thus obtained the amount of phosphorus is estimated, from which the amount of lecithin is then calculated. It sometimes occurs to a remarkably large extent.

L. DE K.

o-Tolidine Sulphates and Titration of Benzidine Sulphate.

JOACHIM BJEVRINGER and WILHELM BORSUM (*Chem. Zeit.*, 1906, 30, 721—722).—A normal sulphate of *o*-tolidine may be obtained by dissolving the base in water with careful addition of dilute hydrochloric acid and then adding excess of dilute sulphuric acid. Instead of acid water, alcohol may be used as a solvent, in which case, however, the sulphate is more finely divided. The compound, when suspended in water, may be readily titrated with standard sodium hydroxide, using phenolphthalein as indicator.

An acid salt may be obtained by mixing carefully a known weight of the normal salt with the required quantity of dilute sulphuric acid, evaporating, and drying at 120°. It is readily dissociated.

Benzidine sulphate may, as is well known, be titrated with sodium hydroxide and phenolphthalein, preferably at 50°. The authors state that the reaction proceeds readily at the ordinary temperature if some barium chloride is added.

L. DE K.

Precipitation and Estimation of Alkaloids with Potassium

Bismuth Iodide. D. JONESCU (*Chem. Centr.*, 1906, i, 1803; from *Ber. Deut. pharm. Ges.*, 16, 130—132).—Not only atropine and hyoscyamine, but also quinine, caffeine, and antipyrine may be precipitated by potassium bismuth iodide and recovered by treating the precipitate with an alkali. Quinine is best extracted with ether and caffeine and antipyrine with chloroform. The latter substance is but very slowly extracted.

L. DE K.

A Reaction for Morphine. C. REICHARD (*Chem. Centr.*, 1906, i,

1465; from *Pharm. Centr.-Halle*, 47, 247—249. Compare *Abstr.*, 1905, ii, 127).—If a trace of morphine or its sulphate or hydrochloride is mixed with a few drops of 35 per cent. formaldehyde and evaporated nearly to dryness, the mass, on being moistened with a drop of stannous

chloride and then gently evaporated, assumes a permanent splendid violet colour. On adding a drop of sulphuric acid, the colour is changed to blue; hydrochloric acid causes fading, whilst aqueous sodium hydroxide turns it reddish-yellow; ammonia has hardly any effect. L. DE K.

A Characteristic Colour Reaction for Morphine. DAN RADULESCU (*Chem. Centr.*, 1906, i, 1378; from *Bull. Soc. Sci. Bucuresci*, 14, 602—605).—For the direct detection of morphine in vegetable infusions, the following test may be employed. The solution, which should be colourless or nearly so, is mixed with a crystal of potassium nitrite; an acid is added, and before the evolution of gas has ceased an excess of strong aqueous potassium hydroxide is added. In presence of morphine, the liquid turns rose or even ruby-red. The colouring matter is not removed by agitation with ether, chloroform, carbon disulphide, or benzene. L. DE K.

Assay of Opium and its Preparations. PHILIP ASHER (*Amer. J. Pharm.*, 1906, [vi], 78, 262—267).—Four grams of dried opium are mixed with 5 c.c. of 5 per cent. potassium hydroxide and dried on the water-bath. Five grams of freshly-slaked lime and 10 c.c. of water are added, and the whole triturated for fifteen minutes. Nineteen c.c. of water are added, and after half an hour, 15 c.c. of the filtrate are collected. To this are added 4 c.c. of alcohol and 10 c.c. of pure ether; the whole is well shaken in a 100 c.c. Erlenmeyer flask, and 0.5 gram of ammonium chloride is added.

After twelve hours, the ethereal layer is poured through a small cotton-wool filter, and the liquid is shaken with another 10 c.c. of ether, and when this has passed through the filter the aqueous liquid is poured on to the filter, and the flask is then rinsed twice in succession with another 5 c.c. of ether. The crystals of morphine are now washed with water saturated with morphine, using 15 c.c. in all. The cotton plug is carefully put back into the flask, and the morphine is dissolved in 12 c.c. of *N*/10 sulphuric acid, the excess of which is then titrated with *N*/40 potassium hydroxide, using a freshly-prepared aqueous solution of hæmatoxylin as indicator.

In the case of tincture of opium, 5 c.c. of potassium hydroxide solution are added to 40 c.c. of the sample, and the mixture is evaporated and then treated with lime as directed. L. DE K.

Separation of Strychnine and Brucine; Influence of Nitrous Acid in Oxidation by Nitric Acid. WILLIAM C. REYNOLDS and ROBERT SUTCLIFFE (*J. Soc. Chem. Ind.*, 1906, 25, 512—515).—Both Stoeder's and Gordin's modifications of the oxidation process (*Abstr.*, 1899, ii, 715; 1903, ii, 342; compare Howard, *Abstr.*, 1905, ii, 779) lead to slightly more trustworthy results than Keller's original process (*Abstr.*, 1903, ii, 342), and of the two Gordin's is the more expeditious. For an amount of total alkaloid up to 0.4 gram, the oxidising solution should contain at least 7 per cent. of nitric acid, the reaction should be stopped after proceeding for ten minutes, and the temperature should not exceed 25°. The strychnine should be liberated by the addition of excess of either potassium or

sodium hydroxide, and not by means of sodium carbonate or ammonia. The nitric acid used should be of sp. gr. 1.42; if more dilute, it is necessary to add a trace of a nitrite to start the reaction. The action of the nitrous acid has not been ascertained, but it appears to be similar to the behaviour of the trace of water vapour necessary to bring about the combination of some gases by the electric spark.

W. P. S.

New Process for Estimating the Casein in Cheese. AUGUSTE TRILLAT and SAUTON (*Compt. rend.*, 1906, 143, 61—63).—The method already described by the authors (this vol., ii, 591) for the estimation of casein in milk can also be applied to the determination of the unchanged casein in cheese; for this purpose, 2 grams of the cheese in a fine state of division are triturated with 10 c.c. of hot water, and 50 c.c. of water added, and the mixture boiled for five minutes; 0.5 c.c. of commercial formaldehyde is then added, and the boiling continued for a further three minutes. The casein is precipitated by five drops of glacial acetic acid, collected on a tared filter, freed from fat by extraction with acetone, dried at 75—80°, and finally weighed. The casein values, thus determined, of various cheeses are as follows: Camembert, 18.20 per cent.; Gruyère, 31.34; Gervais, 6.415; Brie, 22.930; Roquefort (half-ripe), 11.65; Roquefort (very ripe), 7.10; Hollande, 31.5. By this method of estimation the process of ripening of cheese can be determined, thus a freshly-made Roquefort cheese contained 19.48 per cent. of casein; this fell to 18.12, 11.65, 8, and 7.10 per cent. after eight, fifteen, thirty, and sixty days respectively.

M. A. W.

Estimation of Proteid and Gelatinous Matters by means of Acetone. FRÉD. BORDAS and TOUPLAIN (*Compt. rend.*, 1906, 142, 1345—1346).—The insolubility of proteid or gelatinous matter in pure or aqueous acetone can be applied to the determination of the amount present in various food-stuffs. In the case of butter or cheese, the sample is extracted with pure acetone, and the residual casein washed with aqueous acetone, weighed, and then ignited to estimate the ash; in the case of milk, all the proteid matter is completely precipitated by the addition of 20 c.c. of pure acetone to 10 c.c. of the sample, and separation is readily effected by centrifugation.

M. A. W.

Measurement of the Gelatinising Points and Specific Gravities of Solutions of Various Glues. K. WINKELBLECH (*Zeit. angew. Chem.*, 1906, 19, 1260—1262).—The temperature at which the gelatinisation of a given solution takes place is determined by thoroughly shaking 400 c.c. of the solution with a thermometer suspended in it, and cooling the containing flask by immersion in cold water. As the gelatinising point is approached, the solution becomes thicker, air bubbles cease to rise in it, and finally the solution becomes solid. On plotting gelatinising points against the percentage strength of gelatin solutions, continuous curves were obtained, but this was not found to be the case for solutions of glue.

Closely concordant values were obtained for the specific gravities determined by means of either a specific gravity bottle or a hydrometer. It was found that the difference in gelatinising point between glue and good gelatin increases in the case of impure glue with increasing dilution, but remains practically constant in the case of pure glue. P. H.

Fruit of Capsicum Annuum [Chilies]. ANTON NESTLER (*Zeit. Nahr. Genussm.*, 1906, 11, 661—666).—If the dividing walls of the fruit be examined under a lens, small white and brown spots will be seen. These spots are cells filled with a fatty oil (myelin) in which capsaicin is present. On treating a fragment with ammonia on a microscope slide, the well-known spiral threads or loops will be observed to shoot out from the mass. Numerous crystals and groups of crystals can also be seen. When treated with 5 per cent. potassium hydroxide solution, the crystals dissolve, and, after the lapse of a few hours, fine needle-shaped threads are deposited. In the cells of the epidermis and mesophyll are found many colourless crystals; the usual chemical tests prove them to be albumin crystals. Crystals of calcium oxalate are abundant in many specimens of capsicum fruit. Owing to the inactivity of capsaicin towards chemical reagents, the tongue is the best test for this substance. W. P. S.

Calorimetric Assay of Mustard. MANSIER (*J. Pharm. Chim.*, 1906, [vi], 23, 565—573).—The process is devised for comparing the strength of samples of mustard. Fifty grams of the sample are introduced into a calorimeter containing 100 c.c. of water and the increase in temperature due to chemical action is noticed. A second experiment is then made, using 95 c.c. of water and 5 c.c. of a solution of 20 grams of mercuric chloride in 100 c.c. of brine, so as to destroy the action of the ferment, and the increase in temperature is deducted from that in the first experiment.

For a full description of the minute precautions to be taken, the original article should be consulted. L. DE K.

The Process of Decomposition of Pastry. ERICH LEFÈRE (*Zeit. öffentl. Chem.*, 1906, 12, 226—233).—The cause of the decrease in the amount of lecithin-phosphoric acid in pastry, when the latter is stored for some time, is discussed in this paper. Although samples containing excessive quantities of water have been found to give low percentages of lecithin-phosphoric acid, drier samples have also yielded abnormally small amounts. The decomposition of the organic phosphorus compounds is also influenced by the degree to which the pastry has been subdivided. With regard to the whole question of the detection of the presence of eggs in pastry, determinations of any one constituent or analytical constant are of little use by themselves. Flour contains very varying quantities of lecithin-phosphoric acid, the test for cholesterol fails when only small quantities of egg are present, and the acidity of the fat extracted from the sample does not give any useful information. W. P. S.

General and Physical Chemistry.

Measurement of the Wave-lengths of the Iron Spectrum for the Establishment of a System of Spectroscopic Standards. CHARLES FABRY and H. BUISSON (*Compt. rend.*, 1906, 143, 165—167).—Exact measurements of the wave-lengths of about eighty lines in the arc spectrum of iron between the wave-lengths 6500 and 3600 have been made by the photographic method. Each of the lines was compared with the green mercury line as standard, which in its turn was compared directly with the green and red rays of cadmium, for which the values of the wave-lengths given by Michelson and Benoît have been taken as the basis of the calculations. H. M. D.

Band Spectra. JOHANNES STARK (*Chem. Centr.*, 1906, i, 1864; from *Physikal. Zeit.*, 7, 355—361).—In an elementary gas, canal rays produce a line-spectrum and a band-spectrum, of which only the former exhibits the Doppler effect. The sources of the line-spectrum are the positive ions; the band-spectrum is not emitted by either the negative ions or the neutral atoms, but by the positive ions (“Restatome”) and the negative electrons in the act of recombining to form neutral atoms. The motion of the particles emitting the green band-spectrum of mercury vapour is not influenced by an electric field; the same holds true of hydrogen and nitrogen. These particles are, therefore, not charged. The band-lines become blurred by broadening; they cannot be displaced by raising the pressure or the temperature. The different parts of the band-spectrum correspond with different phases of the recombination of negative electrons with positive ions. The distribution of the intensity in the band-spectrum changes, as can be shown experimentally, if the frequency of the different phases of the recombination is altered by change of the temperature. The two kinds of spectra are also compared as regards their absorption.

T. H. P.

Kinetics of Photochemical Reactions. I. Retardation of Photochemical Chlorine Reactions by Oxygen. Relation to Photochemical Induction and Deduction. ROBERT LUTHER and EMANUEL GOLDBERG (*Zeit. physikal. Chem.*, 1906, 56, 43—56. Compare Luther and Weigert, *Abstr.*, 1905, ii, 785).—The experiments of Slator (*Trans.*, 1903, 83, 729) have been expanded, and it is found that the frequently irregular course of the chlorination of benzene under the action of light is due to the retarding effect of small quantities of oxygen. Thus a solution of chlorine in benzene which has been freed from air by boiling out under reduced pressure is twenty times as sensitive to light as a solution in contact with air at atmospheric pressure. Boiling benzene, therefore, is attacked readily by chlorine in diffuse light, not because of the higher temperature, but because the expulsion by boiling of all dissolved air renders the mixture much more sensitive to light. Such a retardation as that

referred to has already been observed in the reaction between chlorine and hydrogen and in that between chlorine and carbon monoxide, and the authors show that the chlorination also of toluene, xylene, and acetic acid is retarded by oxygen. Closer study of the action of chlorine on benzene indicates that any oxygen present at the beginning is gradually removed, and that only after this does the velocity of the main reaction attain its maximum. This period during which the oxygen is being removed may be identified with the so-called "period of induction." The phenomena of "deduction" are probably due to the gradual subsequent collection of a little oxygen from the interaction of chlorine and water, from the walls of the containing vessel, or from leakage through taps. The fact that moist chlorine which has been exposed to light reacts more readily when mixed with hydrogen than chlorine which has not been so exposed may be attributed to the removal during the preliminary exposure of traces of oxygen originally present.

J. C. P.

Observations on Canal Rays. HANS RAU (*Chem. Centr.*, 1906, ii, 293; from *Physikal. Zeit.*, 7, 421—423).—When canal rays impinge on glass, the latter exhibits a green fluorescence and a reddish-yellow surface-layer of light, in the spectrum of which the *D* line is observed. The phenomenon is possibly one of chemiluminescence caused by oxidation, yet it appears in nitrogen quite free from oxygen and, faintly, in almost pure helium. In hydrogen through which the discharge has been passing for a long time, Wien observed only the green fluorescence. If the glass is previously submitted to the action of cathode rays, the action of canal rays does not at first give sodium light, because the cathode rays and the fluorescence produced in the hydrogen by the canal rays produce a chemical change in the surface of the glass. The author explains the illumination observed under the influence of the canal rays as due to intense local heating.

Attempts to measure e/m for helium led to no definite result.

An experiment with canal rays in a strong magnetic field confirmed Stark's view that the positive ions are the emitters of the illumination exhibiting the Doppler effect.

T. H. P.

Retardation of the α -Particle from Radium in passing through Matter. ERNEST RUTHERFORD (*Phil. Mag.*, 1906, [vi], 12, 134—146. Compare this vol., ii, 139).—The velocity of the α -particle from radium C corresponding with each point of its path in air has been determined by measuring the magnetic deflection of the rays after passing through different numbers of layers of aluminium foil of known stopping power. The active wire with a deposit of radium C was placed in a triangular groove in a solid brass cylinder, and above it was placed a parallel slit and a photographic plate, the distances of which from the wire could be varied at will. The photographic impression was measured by projecting a magnified image on a screen by means of an ordinary arc lantern.

It is found that the photographic effect is no longer visible when the α -particle has passed through a layer of foil corresponding with 7.06 cm. of air, the velocity at this point of the path being about 0.4 of the

velocity at emission. If the energy of the particle is represented graphically as a function of the path, the curve obtained, when extrapolated, cuts the axis of abscissæ at a point corresponding with $(7.06 + 1.25)$ cm. of air. From this it is deduced that the ratio of the velocity of a particle of range r to the initial velocity is given by the formula $0.348 \sqrt{r + 1.25}$. Since the ratio of charge to mass is the same for the α -particles from radium, radium A, radium C, and radium F, this formula can be applied to calculate the velocity of the particles emitted by these several substances, and the values deduced agree very satisfactorily with those obtained by experiment.

Examination of the photographic traces indicates a slight scattering of the α -particles in passing through matter. On passing through a mica plate of thickness equivalent to 3.5 cm. of air, a deflection of some of the rays to the extent of about 2° is observed. It is calculated that this change of direction in passing through the 0.003 cm. layer of mica requires an average transverse electric field of about 100 million volts per centimetre.

The author points out that the much more rapid decrease of the photographic effect of the particle towards the end of its path as compared with the decrease in its kinetic energy indicates either the existence of a critical velocity below which it is unable to produce its characteristic effects, or a very rapid decrease in the velocity when this reaches a certain value.

H. M. D.

Influence of Radium Radiations on the Conductivity of Electrolytes. BRONISLAS SABAT (*Bull. Acad. Sci. Cracov*, 1906, 62—79).—The effect of radium radiations on the electrical conductivity of solutions of sodium chloride, calcium chloride, barium chloride, magnesium sulphate, zinc sulphate, potassium carbonate, hydrochloric acid, and sodium hydroxide has been studied. The radium used was 0.2 gram of the strongest radium preparation in a thin-walled glass tube which was placed in the electrolyte.

No immediate effects are noticeable on the introduction of the radium preparation, but after several minutes an increase in conductivity occurs, and gradually attains a maximum; this increase corresponds with that due to the rise in temperature (some 0.3 — 0.4°) produced by the radium radiations. When the radium is removed, the conductivity gradually falls to its normal value.

J. J. S.

Radioactivity of Thorium. JULIUS ELSTER and HANS GEITEL (*Chem. Centr.*, 1906, ii, 302—303; from *Physikal. Zeit.*, 7, 445—452).—From the sediments of the thermal springs of Bad Nauheim and Bad Kreuznach barium containing radium has been isolated, together with a product exhibiting radioactivity similar to, but much more intense than, that of thorium compounds; this product the authors regard as the radiothorium of Hahn (*Abstr.*, 1905, ii, 432 and 789).

The rates of decay of activity of thorium and radiothorium X were compared and found to be approximately equal, from which it is concluded that the activity of thorium depends only on the presence of radiothorium.

T. H. P.

Separation of Radiothorium from Salts of Thorium. G. A. BLANC and OTTORINO ANGELUCCI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 90—94. Compare this vol., ii, 594).—The authors have attempted, by various methods, to separate radiothorium from thorium, the only procedure meeting with any success being the following: thorium nitrate (6 kilos.) was dissolved in water (about 4 litres) and to the solution were added about 60 grams of barium hydroxide and the corresponding quantity of sulphuric acid. No precipitate separated until after the liquid was boiled and agitated vigorously, when about 30 grams of barium sulphate were deposited. After thoroughly washing with water, this precipitate possessed considerable activity, which at first decreased according to the same law as that of thorium X; later on this law was departed from and the activity ultimately became constant at a value small compared with the original one. The radiothorium separated in this way from thorium represents only a small fraction (of the order 0.001) of the total quantity present. T. H. P.

Radioactive Lead extracted from Pitchblende. JEAN DANYSZ, jun. (*Compt. rend.*, 1906, 143, 232—234).—When radioactive lead chloride, extracted from pitchblende, is dissolved in boiling water and precipitated from the cooled solution by means of hydrochloric acid, and this treatment is repeated ten times, the final salt obtained is almost completely inactive, emitting neither penetrating rays nor rays easily absorbable. But these two sorts of rays soon reappear and gradually increase in intensity. This is what should occur, assuming that the whole of the radium E and polonium have been removed from the lead, only the radium D being left; the latter then re-forms radium E, which, in its turn, is transformed into polonium. The penetrating radiation due to radium E should increase according to the law: $I_t = I_\infty (1 - e^{-\frac{t}{\theta}})$, I_t being its value at time t , I_∞ its limiting value (practically attained in a month's time), and θ the time-constant of the radium E. This law assumes a constant production of radium E by radium D.

Experiments made with two different samples give values for θ from 6.51 to 7.12 days, and from 6.25 to 7.43 days in the two cases, the mean values being 6.84 and 6.81 days. This value of θ corresponds with a diminution of radium E to the extent of one-half in 4.72 days.

The total activity, due to radium E and polonium, varies according to a more complicated law; as a function of the time, it is given by the sum of a constant and two exponentials. As the time constant of polonium is great (about 200 days) compared with that of radium E, the curve must be followed for several months in order to determine this constant exactly. T. H. P.

Supposed Radioactivity of Hydrogen Peroxide. OCTAVE DONY and ALICE DONY (*Chem. Centr.*, 1906, ii, 203—204; from *Sep.-Abdr. Sekt. I. Kong. Chem. Pharm. Lüttich*, 1906. Compare Precht and Otsuki, *Abstr.*, 1905, ii, 296, 495).—The formation of hydrogen peroxide by auto-oxidation can be detected much more sharply by photographic means than by the ordinary chemical reactions, a further advantage in

the former case being that there is no introduction of foreign substances, which may modify the reaction.

In the rusting of iron, hydrogen peroxide cannot be detected, even photographically. Potassium chloride, which accelerates the oxidation of iron and, further, increases the stability of hydrogen peroxide, destroys the latter rapidly in presence of rust. The decomposition of hypochlorites in presence of potassium chloride and ferric oxide probably depends on a similar process.

The activating of many organic compounds in presence of radiations more probably depends on formation of hydrogen peroxide. In gelatin the latter diffuses about as rapidly as a salt in water.

Two chambers were arranged, each containing a photographic plate and hydrogen peroxide solution, between which, in one case, a sheet of metal was placed. On passing equal currents of air for the same time through the two chambers, the two plates were found to be blackened to the same extent; this result cannot be explained by the radiation theory of Graetz (*Physikal. Zeit.*, 5, 698). The gelatin exhibits an extraordinarily great absorptive power for hydrogen peroxide vapour.

When vapours of water and hydrogen peroxide act in the dark on a selenium cell, the resistance of the latter falls, owing to a modification produced in the surface of the selenium. The action of hydrogen peroxide on a photographic plate is increased by the addition of substances, such as sulphuric acid, which render the peroxide more stable.

Whether the vapours of hydrogen peroxide exist as such or whether they consist of a modification of oxygen which readily re-forms hydrogen peroxide, is not decided. T. H. P.

Absorption of Nitrogen by Organic Substances under the Influence of Radioactive Matter. MARCELLIN BERTHELOT (*Compt. rend.*, 1906, 143, 149—152).—A piece of filter paper was sealed up in a glass tube containing a small quantity of impure radium chloride. This tube was wrapped in another sheet of paper and enclosed in a second tube, which was then kept in the dark for a period of eleven months. The sealed tube, which originally contained 29.1 c.c. of air, was then found to contain 15.5 c.c. of nitrogen, 1.5 c.c. of carbon dioxide, and no oxygen. 7.6 c.c. of nitrogen and 6.0 c.c. of oxygen had been absorbed by the organic matter. The author points out that this phenomenon is analogous with the absorption already observed under the influence of atmospheric electricity and the silent discharge.

The rays which are effective in promoting the absorption of nitrogen are unable to pass through the glass of the inner tube. The glass of both the inner and outer tubes in the above-described experiment was coloured. The two colour changes are distinct from each other, and are to be attributed to different kinds of radiation. Chemical changes thus lead in the same way as physical measurements to the view that the radiations from radium are heterogeneous. H. M. D.

A Mineral which retards the Discharge of an Electroscope. ERNST H. BÜCHNER (*Chem. Centr.*, 1906, ii, 151—152; from *Chem. Weekblad*, 3, 325—328).—A mineral from the south of Norway, assumed to contain radium, was found to retard the discharge of an

electroscope. The retarding influence appears to diminish with time, and finally gives way to the ordinary acceleration of discharge. It is supposed that, from the beginning, both these influences are at work, the radioactive one producing on the walls of the electroscope an induced activity, which ultimately exceeds the retarding action of the mineral. That no permanent change is here produced in the mineral is shown by the fact that the retarding effect is the same after twenty-four hours. The supposition that the mineral emits positively charged particles is excluded by the observation that it exhibits the same behaviour towards a negatively charged electroscope as towards one positively charged. The neighbourhood of a solution containing radium impairs the activity of the mineral, so that it accelerates the discharge of the electroscope; but when left for a week in surroundings devoid of radium, the substance reverts to its original condition. It is remarkable that, after the mineral has been removed, the velocity of discharge of the electroscope remains the same as during the last measurement of the radioactivity of the mineral. T. H. P.

Relations between the Variation of Electrical Resistance and the Expansion of Monatomic Solids. WITOLD BRONIEWSKI (*J. Chim. phys.*, 1906, 4, 285—310).—During fusion the electrical resistance decreases for those substances which contract on melting and increases for those which expand; this renders it probable that a connection exists between expansion and resistance. Writing the expansion formula $\alpha_t = \alpha_0(1 + Kt)$ as $\alpha_t = \alpha_0[1 + 1/(nF + T_0)t]$, $n = (1 - KT_0)/KF$, where F is the absolute melting point. The values for n for platinum, copper, silver, aluminium, palladium, gold, potassium, and cadmium, as deduced from previous values of the expansion, only vary between 0.94 and 1.13. Considering this as unity the expression above becomes $\alpha_t = (F + T) \times \text{constant}$. For polyatomic substances, n is not unity. Values for the expansion of atomic volume between 6° and the fusion point vary between 0.52 and 0.75, the mean being 0.65, and regarded as constant, whilst the change of atomic volume during fusion is also approximately constant, the mean value being 0.56. The value for the (atomic latent heat of fusion) | (absolute temperature of fusion) is approximately constant, the mean value being 2.37. The author then enunciates the law that "the resistance of monatomic solids varies proportionately to the free space between the particles," and adds a large number of results for the variation of resistance during fusion, and for the temperature-coefficient of the resistance, which are in good agreement with this. L. M. J.

Variation of the Electrical Resistance of Steels near the Transition Points. P. FOURNEL (*Compt. rend.*, 1906, 143, 287—288).—In a previous paper (this vol., ii, 546), the author has shown in the form of a curve the relation between the electrical resistance and temperature for five samples of steel; for temperatures below 600° the curves are arranged on the plane of co-ordinates in the order of the values of Σ , where Σ for each steel is the sum of the products of the carbon, silicon, and manganese content of the steel and the corresponding atomic weight.

Curves representing the relation between the change of electrical resistance with the temperature (dR/dt) and the temperature (t) are given for the five samples of steel; each curve consists of two straight lines, one parallel to the axis of temperature and the other oblique, and for the five curves the temperatures corresponding with the meeting points of the two lines increase as the values of Σ decrease.

Above 900° the resistance increases with the temperature according to the equation $Rt = R_{900}(1 + at)$, the coefficient of variation, a , increasing with Σ . The values of Σ and a for the five samples of steel are appended:

No. of Steel.	Σ .	a .
II	21.14	3.3×10^{-4}
I	31.42	3.3×10^{-4}
IV	33.87	3.8×10^{-4}
V	—	4.0×10^{-4}
III ...	43.36	4.3×10^{-4}

M. A. W.

Atomic Conductivities of the Ions. PHILIP BLACKMAN (*Phil. Mag.*, 1906, [vi], 12, 150—152).—A discussion of the additive nature of the molecular conductivities of acids, bases, and salts. H. M. D.

Conductivity of Mixtures of Electrolytes. III. F. BARM-WATER (*Zeit. physikal. Chem.*, 1906, 56, 225—235. Compare Abstr., 1899, ii, 396; 1904, ii, 10).—When dilute solutions are prepared containing a weak acid and its sodium or potassium salt, or both, the conductivity of the mixed solution can be calculated from the conductivities of the components by the author's formulæ (see *loc. cit.*). The acids used were acetic, propionic, glycolic, and butyric acids. The results bear out the assumptions made, namely, that whilst the influence of the weak acid on the degree of dissociation of the salt is very small, that of the salt on the degree of dissociation of the acid is very great, as required by the theory. J. C. P.

Electrical Conductivity of Colloidal Ferric Chloride. G. MALFITANO (*Compt. rend.*, 1906, 143, 172—174. Compare this vol., ii, 450).—The electrical conductivity of colloidal solutions of ferric chloride is in some cases greater, in others less, than that of the solutions which are obtained by filtration of the former through collodion membranes. The magnitude and sign of the difference depends on the concentration of the solution and on the nature and number of the colloidal granules. It is not possible from the experimental data to assign any definite value to the conductivity due to the granules. H. M. D.

Electrolytic Potential of Certain Peroxides. ARRIGO MAZZUCHELLI and CESARE BARBERO (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 35—42 and 109—113).—The authors have measured the electrolytic potential of peroxides of titanium, vanadium, molybdenum, tungsten, and uranium, and of salts of the hyper-acids and fluohyper-

acids of these elements, peroxides being defined as compounds analogous to hydrogen peroxide, from which they can be prepared by double decomposition, and which they yield on hydrolysis. The measurements were made sometimes in acid and sometimes in alkaline solution, one electrode being of platinum or gold and the other being a normal mercury electrode. The potentials obtained are referred to that of the hydrogen electrode as zero.

It is found that the potentials are not absolutely constant, but vary slightly, both with the time and for different electrodes. The explanation of this behaviour, which has been observed before and may be regarded as a characteristic of the peroxides, is to be found in the capacity possessed by these compounds of acting both as oxidising and as reducing agents, and in the opposed influences thus exerted on the definite potential. The numbers obtained are not in accord with Nernst's formula for the potential, namely, $E = \pi + k \log(C/c)$, where E is the potential and C and c the concentrations of the two degrees of oxidation (normal salt and hyper-salt) present.

Considered from an electromotive standpoint, all the peroxides examined up to the present, with the exceptions of persulphuric acid and Caro's acid, exert by preference a reducing action. All the higher oxides of the elements investigated, from which the peroxides are derived directly, exhibit a more or less marked amphoteric nature; here, too, sulphuric anhydride forms an exception. T. H. P.

Galvanic Polarisation at a Mercury Cathode. GILBERT N. LEWIS and RICHARD F. JACKSON (*Zeit. physikal. Chem.*, 1906, **56**, 193—211).—For their experiments the authors have used a sulphuric acid cell in which the anode was of platinised platinum kept charged with hydrogen. Special care was taken in the purification of the hydrogen, the sulphuric acid, the mercury, and the platinised platinum employed. That the anode in this cell was unpolarisable was shown by the fact that for a given *E.M.F.* applied the current reached a constant value almost immediately; further, the strength (I) of the polarisation current was practically unaffected by moving the contents of the cell, or by increasing the rate of passage of hydrogen over the anode. When the *E.M.F.* applied is gradually raised to 0.7 volt, the corresponding values of $\log I$ lie on a straight line; when the *E.M.F.* applied is then gradually diminished from 0.7 volt, the values of $\log I$ observed all lie above the straight line just described, although not themselves on a regular curve. The fact that the values of $\log I$ observed with decreasing *E.M.F.* lie above those observed with increasing *E.M.F.* indicates that the current itself either produces some substance which catalytically accelerates the electrolytic reaction, or renders the surface of the cathode catalytically active. The theory of the linear relationship between $\log I$ and the applied *E.M.F.* is discussed.

The influence of temperature on the polarisation is not great, and on the whole the authors' experiments indicate that for a given potential the strength of the polarisation current diminishes slightly as the temperature rises.

Experimental evidence shows that the polarisation cannot be

attributed to a homogeneous chemical reaction, or to the diffusion of gaseous hydrogen from the electrode, or to the diffusion of hydrogen ions towards the electrode. It is suggested that the reaction $2\text{H} = \text{H}_2$ may be the process which determines the polarisation, but the authors' work does not supply any definite proof of this view (compare Tafel, *Abstr.*, 1900, ii, 588).
J. C. P.

Dissociation of Nitric Acid in Mixtures of Water and Ether. PETRU BOGDAN (*Zeit. Elektrochem.*, 1906, 12, 489—493. Compare this vol., ii, 83).—Further experiments on the partition of nitric acid between ether and water show that the solubility of water in ether is influenced by the presence of nitric acid except in dilute solutions. The previous conclusions are therefore invalid. Experiments with dilute solutions show that the molecular elevation of the boiling point of ether produced by nitric acid is not independent of the concentration. The solutions conduct electricity. The conductivities of solutions of nitric acid in water saturated with ether are measured; the degree of electrolytic dissociation calculated from them is in agreement with Ostwald's law of dilution, the dissociation constant at 25° being 1.39 .

Assuming that Ostwald's law is true for the dissociation of nitric acid in the ether solutions, a constant coefficient of partition of the undissociated part of the nitric acid is found; the assumption leads to the conclusion that nitric acid dissolved in wet ether is dissociated to a large extent, although the conductivity of the solution is small.

T. E.

Dissociation Constants of Weak Acids. EDMOND BAUER (*Zeit. physikal. Chem.*, 1906, 56, 215—222).—When the absorption coefficients of carbon dioxide in pure water and in solutions of sodium butyrate and sodium benzoate have been accurately determined, it is possible by Sand's method (*Abstr.*, 1904, ii, 612) to calculate satisfactorily the dissociation constants of butyric and benzoic acids. Similarly, the dissociation constant of nitrous acid has been deduced from the absorption coefficient of carbon dioxide in solutions of potassium nitrite, and is found to have the value 6.4×10^{-4} (maximum possible error 8—10 per cent.). A comparison of the conductivities of equally concentrated solutions of potassium chloride and potassium nitrite leads to the value 58 for the ionic conductivity of NO_2' .

J. C. P.

Electrolysis of Alkaline Chlorides. III. Use of Diaphragms of Oxide of Iron. EDOUARD MALLET and PHILIPPE A. GUYE (*J. Chim. phys.*, 1906, 4, 222—231. See *Abstr.*, 1903, ii, 586; 1904, ii, 29).—The ordinary diaphragms in use in electrolysis are not suitable for the electrolysis of alkaline salts, as they are readily attacked and become useless in a comparatively short time, and the concentration of soda in the cathode liquid cannot be raised above about 100 grams per litre. The authors have experimented with diaphragms of a porous oxide of iron, and results of experiments on the porosity, permeability, and use in actual electrolysis are given.

They find this material to be completely unattacked by chlorine or by the alkali, so that highly concentrated cathode liquids can be obtained. Smaller electrolytic vessels may therefore be employed and less evaporation of water required in the manufacture of alkali. L. M. J.

The Law of the Independent Migration of Ions. WILHELM PALMAER (*Zeit. Elektrochem.*, 1906, 12, 509—511).—A simple deduction of the law. T. E.

Model and Experiment to Demonstrate Changes of Concentration during Electrolysis. WILHELM PALMAER (*Zeit. Elektrochem.*, 1906, 12, 511—513).—The model consists of four sets of eighteen beads mounted on horizontal wires. These are supported on fixed vertical supports, which also serve to indicate the boundaries between the cathode, anode, and unchanged intermediate compartments of a Hittorf cell. Two sets of beads serve to mark the initial condition of affairs; the other two sets may be moved in opposite directions, and the beads marked which represent ions which have separated out at the electrodes.

In the experiment, hydrochloric acid (4*N*) is electrolysed in a U-tube with limbs about 70 cm. long; a platinum wire forms the cathode and a silver wire the anode. With 100 volts, the current is about 0.02 ampere. After a few minutes, a difference of level in the two limbs of the tube is observed, due to the changes of concentration of the acid. T. E.

Electrical Conductivity of Solutions in Liquid Iodine. GILBERT N. LEWIS and PLUMER WHEELER (*Zeit. physikal. Chem.*, 1906, 56, 179—192).—The conductivity of solutions of potassium iodide in liquid iodine has been determined at 120°, 140°, and 160°. Liquid iodine, even when it has been purified by sublimation in quartz vessels and has not been brought in contact with glass, appears to have a specific conductivity of about 3×10^{-5} , but further experiments are necessary before the question is definitely settled. Potassium iodide dissolves readily in liquid iodine, and the conductivity of the more concentrated solutions is equal to that of the best conducting aqueous solutions. In the dilute solutions, the molecular conductivity increases in a linear manner with the concentration up to a maximum, after which it falls off. The temperature-coefficient of the conductivity is negative for the dilute solutions, but becomes positive for the more concentrated solutions.

In connection with the abnormal variation of molecular conductivity with concentration, it is noted that in Bancroft's empirical formula for the dilution law, $KC_1 = C_2^n$, n varies for aqueous solutions from 2 for weak acids and bases down to 1.36 for potassium chloride. That is, the greatest deviation from the mass action law is observed when a substance which has itself in the pure state (fused) a high conductivity is added to a solvent which has itself only a slight conductivity. This addition means a change in the dissociating power of the solvent, and it is possible that if a binary salt were added to a solvent with smaller conductivity than water the deviations from the

mass action law would be still more marked and n would have a value less than 1. In such a case, the molecular conductivity would increase with the concentration.

J. C. P.

Pseudo-acids and Amphoteric Electrolytes. ARTHUR HANTZSCH (*Zeit. physikal. Chem.*, 1906, 56, 57—64).—A reply to Lundén's criticism (this vol., ii, 265).

J. C. P.

Colloidal Nuclei and Ions in Dust-free Air saturated with Alcohol Vapour. CARL BARUS (*Amer. J. Sci.*, 1906, [iv], 22, 136—142).—The phenomena of fog formation in supersaturated mixtures of ethyl alcohol and air have been examined and compared with the results obtained in the case of water-air and water-carbon dioxide mixtures. The first medium behaves as if the nuclei were larger than in the case of the last two, and the number of nuclei in alcohol vapour is about 3.5 times as great as for water vapour under like conditions. From the amount of alcohol precipitated per c.c. by the sudden cooling incident on expansion, the number of nuclei corresponding with a given corona has been calculated. Curves are given which show the dependence of the number of nuclei on the fall in pressure and also the effect of subjecting the vapour to Röntgen radiation. The difference between the behaviour of the mixtures alcohol-air, water-air, and water-carbon dioxide is clearly seen by means of these curves.

H. M. D.

Ionisation of Saline Vapours. GEORGES MOREAU (*Ann. Chim. Phys.*, 1906, [viii], 8, 201—242. Compare Abstr., 1903, ii, 125, 196; 1904, ii, 536; 1905, ii, 9; this vol., ii, 68, 217).—On heating a salt of an alkali metal at a high temperature, it undergoes ionisation, and the density of the charges separated is proportional to the square root of the concentration of the salt in the gaseous medium containing it. This law, which Arrhenius found to hold in the case of flames, is also valid at lower temperatures.

The charges at a distance from the region of ionisation constitute the nuclei of ions of which the mobility falls with the temperature and with an increase in the concentration of the salt. The variation of the mobility is explained by the attraction of the charged centres for the saline particles which exist in the gaseous medium, the number of which increases as the saline vapour condenses owing to the lowering of temperature.

Between 0° and 170° the ions have an appreciable mass, which lies between that of the large ions due to the oxidation of phosphorus and that of those produced in the air by Röntgen rays. At the high temperature of a flame, their mass is much smaller. The positive ion with a magnitude of 1 mol. and the smaller negative one consist at first of a corpuscle, which afterwards becomes charged with the saline particles also existing in the flame.

The recombination of the ions proceeds according to the law of mass action, the coefficient of recombination varying inversely with the concentration. This result is justified by the fact that the ions which

recombine are sufficiently heavy for the majority of the collisions to be followed by recombination.

A study of the energy of ionisation shows that the separation of the charges starting from one saline molecule is analogous to the chemical dissociation of ordinary gases. It is found that the heat of ionisation is independent of the state of chemical agglomeration of the salt or of the ionised substance, which indicates that the ionisation is of a corpuscular nature. One molecule of the salt first loses a negative particle which serves as a centre for the negative ion, whilst the rest of the molecule constitutes the positive nucleus. As ammonium salts and acid solutions are only feebly ionised compared with the alkali salts, it seems probable that the negative particle parts the more readily from the alkali metal.

The author's results thus confirm the hypothesis of the theory of flame, that a corpuscular radiation takes place from the metallic atom.

T. H. P.

Diminution of the Mobility of Ions in Fog. JULIUS ELSTER and HANS GEITEL (*Chem. Centr.*, 1906, ii, 200; from *Physikal. Zeit.*, 7, 370—371).—Air charged with fog possesses a relatively low conductivity owing to the ions being less mobile. This fact is employed by the authors in demonstrating the positive self-electrification of radium during the emission of β -rays.

The authors have also observed the volume charge appearing in the air when the ions are kept in a layer of mist. Carbon dioxide, charged with ammonium chloride vapour, was passed into an earthed metallic dish over which was fixed a charged metallic plate. When a source of ions was placed between the plate and the dish the vapour became charged in the same sense as the plate. After removing the source of the ions the plate was earthed and the dish connected with the electrometer; on blowing the ammonium chloride vapour suddenly from the dish the electrometer indicated a charge opposite in sign to that of the plate.

Layers of fog or mist resting on the ground exhibit in the normal electric field of the earth a positive volume charge.

T. H. P.

The Mean Path traversed by Gaseous Molecules and its Relation to the Theory of Diffusion. MARIE SMOLUCHOWSKI (*Bull. Acad. Sci. Cracow*, 1906, 202—213).—A mathematical discussion of the mean free path of a gaseous molecule and the application to the elaboration of a mathematical formula for gaseous dissociation.

J. J. S.

The Electro-capillary Function. LÉON G. GOUY (*Ann. Chim. Phys.*, 1906, [viii], 8, 291—363).—A detailed account of work already published (*Abstr.*, 1901, ii, 83, 435, 592; 1902, ii, 194, 487).

M. A. W.

Electric Vacuum Furnace. WILLIAM C. ARSEM (*J. Amer. Chem. Soc.*, 1906, 28, 921—935).—An electrical resistance furnace enclosed in a vacuum chamber and cooled by a water-jacket is described and

figured. The parts liable to be injured by excessive heating are also cooled by a current of water. The furnace is provided with a mica window through which the effect of heat on any substance or reaction may be observed up to the vaporising point of carbon. The heater consists of a helix of carbon or graphite; for high temperatures artificial graphite is to be preferred; it is surrounded by a radiation screen made of a double-walled cylinder of graphite packed with graphite powder. With this screen in position, the melting point of platinum is reached with a quarter of the electrical energy necessary without it. The life of the heater shortens rapidly at high temperatures: nine hours at 2500° , three-quarters of an hour at 3100° , in consequence of increasing vaporisation of carbon from its centre. The substance to be heated is placed in a crucible of graphite for high temperatures, of magnesium oxide for the fusion of metals or the preparation of alloys below 1650° , or of iron, copper, fire-clay, porcelain, or thorium oxide for special purposes. To prevent the formation of cracks, the magnesium oxide crucibles must be fired at 1350° .

The relation of the temperature to the electrical energy was determined by observing the kilo-volt-amperes necessary to maintain the furnace at the melting points of pure copper and platinum respectively. From the results is obtained the expression: $y^n = ax$, in which y is the temperature of the furnace above that of the room, x is the energy in kilo-volt-amperes, and n and a are constants for which the values 1.895 and 285,200 respectively are calculated. The relation of the temperature to the electrical energy is given also in the form of a curve.

G. Y.

Method for Determining the Temperature and Conductivity for Heat of the Positive Column. J. E. LILIENFELD (*Chem. Centr.*, 1906, ii, 200; from *Ber. deut. Phys. Ges.*, 4, 182–196).—Good conducting, and therefore dissociated, gases should possess a high conductivity for heat, and the author describes an arrangement by means of which the process of dissociation can be studied in this way. The discharge is made to pass between two large electrodes placed between two glass bulbs connected by a capillary tube. In the capillary is placed a thin platinum strip, to which a known amount of heat is imparted electrically; the constant temperature assumed by this strip is measured electrically. When introduced into the column, the strip does not assume the temperature of the gas, but remains considerably cooler than the latter. The heat conductivity in the positive column is always higher than the normal value under similar conditions. In hydrogen, the heat conductivity and temperature are always higher than in oxygen or nitrogen.

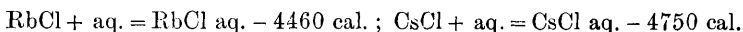
T. H. P.

Researches on the Thermic and Electric Conductivity Power of Crystallised Conductors. FRANS M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 89–98).—Since it has been found that the quotient of the electric and thermal conductivities of all metals is a constant, independent of their chemical nature, but directly proportional to the absolute temperature, it seemed probable that this ratio should also be constant for these properties measured parallel to the

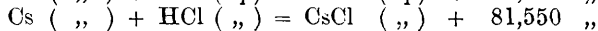
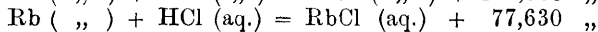
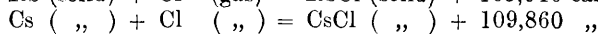
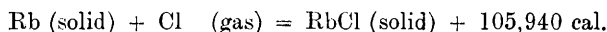
three axes of the crystal. This supposition has been tested on crystalline bismuth and hematite. In neither case was this ratio found to be constant. The bearings of the results on the theory of crystalline structure are discussed.

K. J. P. O.

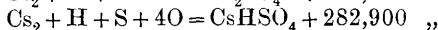
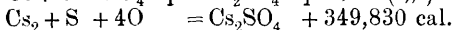
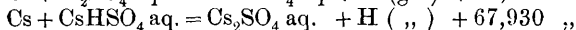
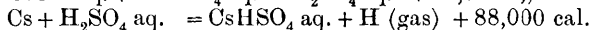
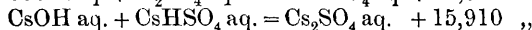
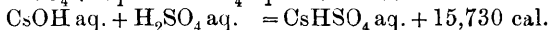
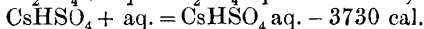
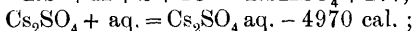
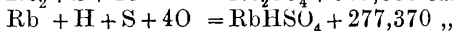
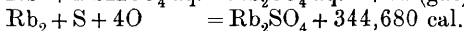
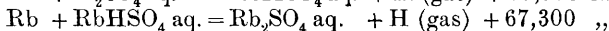
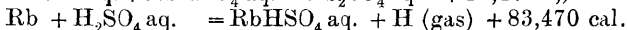
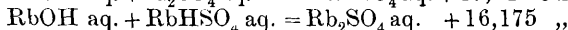
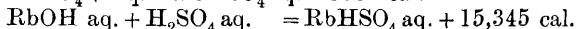
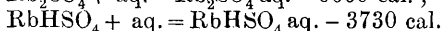
Chlorides and Sulphates of Rubidium and Cæsium. ROBERT DE FORCRAND (*Compt. rend.*, 1906, 143, 98—101. Compare this vol., ii, 445).—The following thermochemical data have been determined :



Assuming that the heat of neutralisation of the bases is the same as that of potassium hydroxide, the author obtains :



The heat development in the formation of the chlorides increases regularly with the atomic weight in the series, sodium, potassium, rubidium, cæsium.



As in the case of the chlorides, the thermochemical data for the sulphates of the metals Na, K, Rb, Cs form a regular series. If the data for lithium, calcium, strontium, and barium are compared, the differences are small, and lithium, with the smallest atomic weight, appears to stand between calcium and strontium.

H. M. D.

Three-phase Lines in Chloral Alcoholate and Aniline Hydrochloride. HENDRIK W. BAKHUIS ROOZEBOOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 99—104).—[With LEOPOLD.]—Three-phase lines should be observed in the case of solid compounds, the liquid phases of which dissociate into two substances of differing volatility. In many cases, such as ammonium hydrosulphide, the liquids are only formed at such high pressures that the course of the three-phase line cannot be

studied experimentally. Both chloral alcoholate and aniline hydrochloride are well adapted to the investigation. Further, the liquid mixture of the two dissociated products shows a minimum vapour pressure. In both cases the three-phase line has been followed and its relation to the sublimation line and to the vapour pressure line of the undissociated compound determined.

K. J. P. O.

Improved Condensation Apparatus. H. E. BARNARD and H. E. BISHOP (*J. Amer. Chem. Soc.*, 1906, **28**, 999—1002).—The authors describe and figure a cheap and convenient arrangement of condensers of metal tubing and gas fittings allowing of a number of distillations being carried on simultaneously. Space is economised by slanting the condensers; these are supported by central swivels and may be rotated to facilitate the removal of the distillation flasks.

G. Y.

Experimental Determination of the Surface Tension of Liquid Oxygen and of Liquid Nitrogen. LEO GRUNMACH (*Sitzungsber. K. Akad. Wiss. Berlin*, 1906, 679—686).—Using a method previously described (Abstr., 1901, ii, 646), the surface tensions of liquid oxygen and liquid nitrogen have been determined.

The oxygen boiled at -182.65° at 762.22 mm., a value in closer agreement with Holborn's than with Dewar's value. Four series of observations were made, from which the mean value 13.074 ± 0.066 dyn./cm. was found. The specific cohesion is 23.038.

The liquid nitrogen boiled at -195.9° under a pressure of 749.1 mm., its surface tension was 8.514 ± 0.02 dyn./cm., and its specific cohesion 21.527.

The molecular weights were calculated from the equation :

$$M = \sigma \sqrt{(2.227\{\theta - T\}/a)^3}.$$

For oxygen the mean value 41.51 and for nitrogen the value 37.30 were found. Both these liquids seem therefore to be associated, whereas it was previously found that the compounds ammonia, sulphur dioxide, and nitrous oxide had the same molecular weights in the liquid and the gaseous states.

K. J. P. O.

A Rule for Capillary Phenomena analogous with Trouton's Rule for the Latent Heat of Evaporation. WLADIMIR A. KISTIAKOWSKY (*Zeit. Elektrochem.*, 1906, **12**, 513—514).—For 40 non-associating liquids the value of $\alpha.M/T$ is shown to lie between 0.0101 and 0.0119, the mean being 0.0116. In the formula, α is the height to which the liquid would rise in a tube 1 cm. in diameter at its boiling point, M is the molecular weight, and T the absolute boiling point.

Associating liquids give smaller values for the constant; water and acetic acid, for example, give normal values when a double molecular weight is taken.

T. E.

Pressure in the Capillary Layer Parallel to its Surface. GERRIT BAKKER (*Zeit. physikal. Chem.*, 1906, **56**, 95—104. Compare Abstr., 1905, ii, 304).—A theoretical paper.

J. C. P.

Influence of Other Substances on the Rate of Diffusion in Jellies. HEINRICH BECHHOLD and J. ZIEGLER (*Zeit. physikal. Chem.*, 1906, **56**, 105—121).—The rate of diffusion of electrolytes and non-electrolytes in gelatin and agar-agar diminishes as the percentage strength of the jellies increases. The authors have studied the rate of diffusion of some colouring matters and electrolytes into gelatin and agar-agar jellies containing various other substances. The permeability of these jellies is diminished by the presence of sodium sulphate, dextrose, glycerol, and alcohol, but is generally increased by the presence of carbamide. Sodium chloride and iodide appear to be without any very definite influence on the permeability of the jellies.

The effect of electrolytes and non-electrolytes on the melting points (determined under similar conditions) of gelatin and agar-agar jellies is irregular in character. Thus, in contrast with the behaviour of gelatin, the melting point of agar-agar is lowered by dextrose and glycerol, but raised by sodium chloride. J. C. P.

Solubility of Sparingly Soluble Substances. II. Solubility of Silver Chloride, Bromide, and Thiocyanate at 100°. WILHELM BÖTTGER (*Zeit. physikal. Chem.*, 1906, **56**, 83—94. Compare Abstr., 1904, ii, 241).—The conductivity of saturated solutions of the salts named has been determined in the apparatus used by Noyes and Coolidge (Abstr., 1904, ii, 226). From the values of the conductivity, the solubilities have been calculated in the usual way. The values thus obtained for the solubility at 100° (expressed as milligrams of salt per litre of saturated solution) are as follows: silver chloride, 21.8; silver thiocyanate, 6.4; silver bromide, 3.7. It thus appears that the washing of silver chloride precipitates with hot water may result in perceptible loss if large quantities of water are used. The relative increase of solubility between 20° and 100° is not so great in the case of the chloride as in the case of the other two salts. J. C. P.

Solubility of the Chlorates, Bromates, and Iodates of the Alkaline Earth Metals. I. Barium, Chlorate, Bromate, and Iodate. MAX TRAUTZ and ARNOLD ANCHÜTZ (*Zeit. physikal. Chem.*, 1906, **56**, 236—242).—The solubilities of the three barium salts have been determined at points between the cryohydric temperature and the temperature of the saturated boiling solution. A few of the solubility values (in grams of anhydrous salt per 100 grams saturated solution) are given in the following table:

	0°.	20°.	50°.	90°.
Barium chlorate	16.9	25.26	36.69	48.7
Barium bromate	0.29	0.65	1.72	4.26
Barium iodate	0.008	0.022	0.056	0.141

In all cases, the solid in equilibrium with the saturated solutions is the monohydrate. J. C. P.

Influence of One Substance on the Solubility of Another. ROBERT RIEDEL (*Zeit. physikal. Chem.*, 1906, **56**, 243—253).—The partition coefficient of aniline between toluene and water varies with

the concentration, and it is suggested that aniline, when dissolved in toluene, may exist partly as single and partly as double molecules, the relative proportions of these varying with the concentration. The influence which inorganic bases (barium, strontium, and calcium hydroxides) have in lowering the solubility of aniline in water is greater than the corresponding influence of salts, and increases with the strength of the base.

J. C. P.

Miscibility of Crystallised Phases. FRANS M. JAEGER (*Zeit. Kryst. Min.*, 1906, 42, 236—276).—Numerous examples are collected together and discussed, and several new observations added of cases in which organic compounds of different kinds are capable of forming mixed crystals or solid solutions. It is concluded that the greater the similarity between the spacial crystalline structure of the two substances the greater is the extent to which they can form mixed crystals. The conclusions of G. Bruni and others (*Abstr.*, 1903, ii, 63, 715; 1904, ii, 388, 712; 1905, ii, 153) as to the isomorphism of such substances are adversely criticised.

L. J. S.

Formation of Complexes, Hydration, and Colour. GILBERT N. LEWIS (*Zeit. physikal. Chem.*, 1906, 56, 223—224. Compare *Abstr.*, 1905, ii, 509; Donnan, *ibid.*, ii, 806).—The author admits that Donnan and Bassett's experiments establish the existence of a complex anion in blue cobalt chloride solutions, but contends that the colour change from blue to red must be in some way associated also with a process of hydration.

J. C. P.

Researches on Chemical Equilibria. E. BRINER (*J. Chim. phys.*, 1906, 4, 267—284).—The results of the work have been previously published (this vol., ii, 424, 529). The present paper contains also an account of the author's work on the system $\text{SO}_2 + \text{NH}_3$. Contrary to usual statements, the compound $\text{SO}_2(\text{NH}_3)_2$ was never obtained. It was found that the action was not reversible, the probable cause of this being the partial reduction of the sulphur dioxide to sulphur.

L. M. J.

Chemical Equilibrium of Several Bases exposed simultaneously to the Action of Phosphoric Acid. MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1906, [viii], 8, 289—290).—A reply to Quartaroli (compare *Abstr.*, 1905, ii, 821; and Berthelot, *Abstr.*, 1901, ii, 504; 1902, ii, 255).

M. A. W.

Reactivity of Certain Acids in Alcoholic Solutions. EMIL PETERSEN (*Chem. Centr.*, 1906, ii, 228; from *K. Dansk. Vidensk. Selsk. Forh.*, 1906, 41—66).—The method of working adopted by the author was to dissolve the acid in a large proportion of alcohol contained in a small flask having a narrow neck; the latter having been fused up, the flask was heated for a definite time at 100° , and then rapidly cooled, the contents being titrated with $N/40$ or $N/80$ barium hydroxide solution.

The reaction between hydrochloric acid and much methyl alcohol is

not strictly unimolecular, the order of the reaction being between 1 and 2. With ethyl alcohol and hydrochloric acid, however, the reaction is strictly unimolecular, and the constants are independent of the concentration of the acid, which is not the case with methyl alcohol; in both instances, the addition of water greatly diminishes the velocity of the reaction. The author deduces the equation for a reaction of the first order with diminishing amounts of catalyst.

Measurements were made of the velocities of reaction of the first six fatty acids in *N*/10 solution with a large excess of alcohol and in presence of a little hydrochloric acid. The reactions are all of the first order. Formic acid acts considerably more strongly than the others, for which the constants, corrected for the hydrochloric acid, are as follows:

		Methyl alcohol.	Ethyl alcohol.
Acetic acid	54	7.8
Propionic	„	44	5.5
Butyric	„	24	3.6
isobutyric	„	20	2.2
Valeric	„	9	3.5

The salt-forming reactivities of these acids in alcoholic solution were determined by Ostwald's volumetric chemical method, the distribution of sodium between each acid and dichloroacetic acid being measured. The reactivity is found to be the same for each of the five acids. When 1 gram-mol. of the salt of the fatty acid is mixed with 1 gram-mol. of the dichloroacetate in about *N*/5 concentration, 95.4 per cent. of the former salt is in all cases decomposed.

T. H. P.

Mechanism of the Reduction of Potassium Permanganate. Kinetics of the Reaction between Potassium Permanganate and Formic Acid. ANTON SKRABAL and J. PREISS (*Monatsh.*, 1906, 27, 503—542. Compare Skrabal, *Abstr.*, 1905, ii, 17).—The mechanism of the reduction of potassium permanganate is independent of the nature of the reducing agent. Thus the oxidation of formic acid by potassium permanganate takes place in stages similar to those of the oxidation of oxalic acid. An incubation period is distinctly observable in the action of manganese peroxide as well as of potassium permanganate on formic acid.

The oxidation of formic acid by tervalent manganese is the only reaction which can be said with certainty to take place without acceleration of the original velocity. Manganic ions which are formed in the first stage of the action of the higher oxides of manganese, as also of manganese salts, react more rapidly with formic acid than does manganese in any other degree of oxidation. The reaction of manganese salts with formic acid is a reaction of the first order and the velocity coefficients are constant only when the concentration of the formic acid is constant. Within the limits of the measurable reaction, the velocity of the oxidation is proportional to the original concentration of the formic acid.

An incubation period is observed also in the spontaneous decompo-

sition of potassium permanganate, during which oxygen is evolved (compare Vorländer, Blau, and Wallis, this vol., i, 730).

G. Y.

Esterification of Benzoic Acid by means of Alcoholic Hydrogen Chloride. ANTON KAILAN (*Monatsh.*, 1906, 27, 543—600).—The author has repeated the work of Goldschmidt (Abstr., 1896, i, 229; ii, 638) on the esterification of benzoic acid by means of alcoholic hydrogen chloride at 25°, but with wider variations in the concentration of the reacting substances. If the esterification of benzoic acid in absolute alcoholic solution is calculated as a unimolecular reaction, the velocity constant k is found to diminish markedly as the reaction proceeds if the concentration of the benzoic acid is comparatively high. This is caused, as stated by Goldschmidt, by the change in the nature of the solvent consequent on the formation of water during the reaction, and not by hydrolysis of the ester formed by the water or hydrogen chloride. If the concentration of the benzoic acid is small, the diminution of k is negligible.

The relation of the velocity of esterification to the concentration of the hydrogen chloride, as given by Goldschmidt, is found to apply only to solutions in 99.85 per cent. alcohol; in alcoholic solutions containing a larger proportion of water, the velocity constant k increases more rapidly than the concentration of the hydrogen chloride. In alcoholic solution containing 3 gram-mols. of water per litre, k was found to vary during the reaction, but not in one direction only.

The relation of the velocity constant to the concentration of the hydrogen chloride and to the amount of water present is represented by the expression: $1/k = 5.78 + 13.24/c + (-35.36 + 59.26/c - 4.778/c^2 + 1.707/c^3)w + (16.98 - 24.80/c + 38.35/c^2 - 3.679/c^3)w^2$, which applies to solutions in which the molecular concentration of the water lies between $w = 0.02$ and $w = 2.25$, and that of the hydrogen chloride between 0.15 and 0.8 or 1.0; with $2/3N$ hydrogen chloride, the expression applies also to solutions with $w = 6$. For a given concentration of the hydrogen chloride, the equation representing the velocity of esterification takes the form: $t_2 - t_1 = [a + \beta(A + w_0) + \gamma(A + w_0)^2] \log(a - x_1)/(a - x_2) - 1/2 \cdot 3026 \{ [\beta + \gamma(A + 2w_0)](x_2 - x_1) + \gamma/2(x_2^2 - x_1^2) \}$, in which x is the number of gram-mols. of the ester formed per litre at the time t . It is shown that the relation of the velocity constant to the amount of water present explains the course of the reaction with the higher concentrations of benzoic acid.

The ester formed when the reaction is prolonged must assist in the retardation of the velocity of the esterification, as k is slightly diminished if small amounts of ethyl benzoate are added to the reacting mixture. If the alcohol is not cooled during the addition of the hydrogen chloride, the constant k as observed is too small in consequence of the presence of water formed together with ethyl chloride.

G. Y.

Kinetics of the Transformation Thiocarbimide \rightarrow Ammonium Thiocyanate in Dilute Aqueous Solution. PAUL DUTOIT and LÉON GAGNAUX (*J. Chim. phys.*, 1906, 4, 261—266).—The reaction in $N/10$ aqueous solution was found to proceed normally as a unimolecular reaction; the constant value of k was found to be 0.0195 at 176.2° , 0.0167 at 175° , 0.00465 at 161.1° , and 0.00099 at 148.5° , giving a temperature-coefficient of 2.9 per 10° . Small quantities of sodium hydroxide cause a decrease in the velocity, whilst sulphuric acid causes an increase, the effect, however, being small in both cases. At the temperature of 123.4° the values of k decrease rapidly, probably indicating that the reaction tends to a measurable equilibrium.

L. M. J.

Velocity of Autoracemisation of Optically-active Ammonium Salts. EDGAR WEDEKIND (*Zeit. Elektrochem.*, 1906, 12, 515—516; Hans Goldschmidt, *ibid.*, 1906, 12, 516—517).—Polemical (compare this vol., i, 419; ii, 612).

T. E.

A Property of Enzymes. JACQUES DUCLAUX (*Compt. rend.*, 1906, 143, 344—346).—A theoretical paper. The diastatic properties of a colloid depend not so much on the total mass of colloid present as on the part of it which is active, thus in the case of colloidal ferric hydroxide, $\text{Fe}_2\text{O}_3, m\text{Fe}_2\text{Cl}_6$, which in the presence of hydrogen peroxide possesses diastatic properties, the active part here is the $m\text{Fe}_2\text{Cl}_6$, and the value of m varies with the electric sign of the colloid, its coagulation, and the absorption of dissolved substances by the colloid (compare Abstr., 1904, ii, 162, 243, 325; 1905, ii, 432, 511; this vol., ii, 677).

M. A. W.

Influence of Non-electrolytes on the Mutual Precipitation of Colloids of Opposite Electrical Sign. J. LARGUIER DES BANCELS (*Compt. rend.*, 1906, 143, 174—176).—The formation of a precipitate on mixing solutions of colloidal ferric hydroxide and aniline-blue in the presence of various non-electrolytes such as carbamide, glycerol, ethyl alcohol, formaldehyde, acetone, dextrose, and sucrose has been examined. It is found that carbamide facilitates the precipitation, whilst the other non-electrolytes have the opposite effect, ethyl alcohol, formaldehyde, and acetone being most active in this respect.

H. M. D.

Isomorphism of Potassium Chlorate and Nitrate. JEAN HERBETTE (*Compt. rend.*, 1906, 143, 128—130).—Experiments have been made to determine whether potassium chlorate is capable of forming mixed crystals with the ordinary rhombic form of potassium nitrate. On evaporation of a solution containing 15 grams of chlorate and 100 grams of nitrate, two kinds of crystals separate. The one kind is monoclinic and contains 65 per cent. of chlorate, the other is rhombic and consists of pure nitrate. Thus, whilst the unstable form of potassium nitrate is apparently isomorphous with the ordinary form of the chlorate, there appears to be no second form of the chlorate isomorphous with the stable form of the nitrate. This

fact may be utilised in a practical way for the separation of dimorphous substances by crystallisation.

Angular measurements of the mixed crystals obtained by slow evaporation show that the crystallographic properties are by no means intermediate between those of the pure substances. H. M. D.

The Atomic Weights of all Chemical Elements are Commensurable and Matter is Uniform. GUSTAV D. HINRICHS (*Chem. Centr.*, 1906, ii, 197; from *Mon. Sci.*, [iv], 20, i, 419—436. Compare this vol., ii, 450).—The author discusses critically the development of the estimation of atomic weights during the three periods of Berzelius, Dumas, and Stas. The value 12 for carbon is taken by the author as the starting point of his system. A number of cases are discussed in which the author states that incorrect fractional atomic weights have been arrived at, and in which the application of the author's method yields integral values. The author assumes that all elements are composed of a primordial element, pantogen.

Crookes's value for thallium becomes 204.00 when the true number for nitrogen is taken. Similar considerations hold for boron, sodium, arsenic, and platinum. Chlorine, 35.5, and copper, 63.5, are the only elements with non-integral atomic weights. It is concluded that all atomic weights are multiples of 0.5. T. H. P.

Basis of Stoichiometry. EMIL BAUR (*Zeit. anorg. Chem.*, 1906, 50, 199—209. Compare Ostwald, *Trans.*, 1904, 85, 506—522).—Mainly polemical against Benedicks (this vol., ii, 530). The author contends that the objections raised by the latter to Ostwald's deductions of the stoichiometrical laws are groundless. It is shown, in agreement with Ostwald, that the law of combining weights can be deduced with the help of the theory of coexistence of phases, and the author offers an alternative deduction based on entirely different premises (the theory of simultaneous equilibrium). G. S.

Lecture Experiments. [Densities of Oxygen and Hydrogen. Structure of Flames. Effect of Substituents in the Benzene Nucleus.] JOHANNES THIELE (*Annalen*, 1906, 347, 140—142).—The relative densities of hydrogen and oxygen are demonstrated by taring two evacuated glass bulbs whose volumes are in the proportion of 1 to 16, filling the larger with hydrogen and the smaller with oxygen, and showing on the balance that no change of weight occurs.

A simple means of showing the structure of a flame by means of the mantle of an incandescent gas burner is described.

The effect of the position of nitro-groups on the basicity of nitroanilines is readily demonstrated by pouring solutions of the three nitroanilines in a little concentrated sulphuric acid into water; the *o*-nitroaniline is mainly precipitated, the solution becoming colourless; the solution of *p*-nitroaniline becomes yellow; the solution of the *m*-nitroaniline remains colourless. K. J. P. O.

Chemical Lecture Experiments. [Reduction of Calcium Carbonate. Ignition of Calc Spar. Oxidation of Iron. Carbon Dioxide.] FRANZ KÜSPERT (*Chem. Centr.*, 1906, ii, 87—88; from *Zeit. phys.-chem. Unterr.*, 19, 166—167).—Reduction of calcium

carbonate (limestone) with powdered magnesium gives amorphous carbon, which is rendered visible by treating the mass with dilute hydrochloric acid.

When a cleavage rhombohedron of calcspar is heated on an asbestos dish with the blowpipe flame, the lime formed retains the shape of the original crystal, so that it can be weighed and the proportion of carbon dioxide lost thus estimated.

The necessity for protecting molten iron in the blast furnace by means of slag may be shown by placing a small piece of glowing wood-charcoal on the surface of purified iron-filings, and then directing a vigorous stream of oxygen on to the latter. The whole fuses to a mass of ferroso-ferric oxide, which remains white-hot for some time after the withdrawal of the oxygen current.

Carbon dioxide can be obtained from an inverted soda-water syphon. A litre syphon, filled at a pressure of 7 atmospheres, yielded 3.5 litres of the gas.

T. H. P.

A New Porcelain Filter. WILLIAM BULLOCH and J. A. CRAW (*J. Hygiene*, 1906, 6, 408—420).—A new filter, for bacteriological purposes, is fully described and figured.

W. D. H.

Separating Apparatus for Heavy Liquids. ERICH KAISER (*Centr. Min.*, 1906, 475—477).—The glass apparatus, to be used for separating mineral particles with the aid of heavy liquids, consists of two cylindrical portions connected by a tap, the bore of which is the same as that of the whole tube. The stoppers at the upper and lower ends of the tube also serve the purpose of supports for the apparatus, and as troughs for collecting the heavy liquid.

L. J. S.

Inorganic Chemistry.

Some Reactions of Liquid Chlorine. VICTOR THOMAS and P. DUPUIS (*Compt. rend.*, 1906, 143, 282—284).—Liquid chlorine reacts with iodine to form iodine trichloride, and, as it is almost insoluble in excess of chlorine, this forms a convenient method of preparation; the same compound is also formed together with the chloride of the metal by the action of liquid chlorine on certain metallic iodides. Bromine reacts with liquid chlorine to form the monobromide BrCl , which solidifies at -39° , and combines with more chlorine to form a higher chloride, probably BrCl_3 ; this is a red solid at -79° , boils at -19° , and decomposes below 0° .

Sulphur does not combine with liquid chlorine, but selenium and tellurium yield their respective di- and tetra-chlorides, and sulphur dioxide is converted into sulphuryl chloride.

Chlorine at its boiling point reacts with arsenic with incandescence to form arsenic trichloride, but it has no action on antimony or bismuth, attacks gold very slowly, and converts thallic chloride into

the sesquichloride, no higher chloride being formed (compare this vol., ii, 356). Liquid chlorine is without action on carbon disulphide, lead or manganous chloride, or potassium permanganate. M. A. W.

Influence of Pressure and of the Form of the Discharge on the Production of Ozone. ANTOINE CHASSY (*Compt. rend.*, 1906, 143, 220—222).—The amount of ozone formed by the electric discharge, acting for a given very short time, decreases with, but much less rapidly than, the pressure of the oxygen. Thus, at a pressure of 100 mm. this initial amount of ozone formed is about half that obtained at 760 mm. pressure. If the action of the discharge is continued, the concentration of ozone increases, the rate of increase being less at the lower pressure. Indeed, the limiting concentration corresponding with any given temperature diminishes, although slightly, with the pressure.

No ozone is produced at pressures lower than about 60 mm., no matter what the duration of the experiment may be. Further, at these low pressures, the discharge produces a uniform light similar to that formed in a Geissler tube only moderately evacuated. If ozonised oxygen is rarefied, it is found that, in the absence of any electrical influence, it is as stable at pressures less than 60 mm. as at the ordinary pressure; but if the rarefied gas is subjected to the action of the discharge, the ozone present is transformed into ordinary oxygen.

T. H. P.

Preservative Action of Sodium and Calcium Chlorides on Hydrogen Peroxide Solutions. L. ALLAIN (*J. Pharm. Chim.*, 1906, [vi], 24, 162—165).—A table is given showing that hydrogen peroxide solution is decomposed less readily if kept in a yellow instead of a white or blue bottle. The decomposition proceeds about ten times more slowly when 10 grams of sodium or calcium chloride per litre is added than when the customary quantity of alcohol or sulphuric or phosphoric acid is added. The solution is best preserved by using sodium chloride and storing in a yellow bottle.

L. DE K.

Vapour Pressure of Sulphur. W. MATTHIES (*Chem. Centr.*, 1906, ii, 204; from *Physikal. Zeit.*, 7, 395—397).—The following boiling points of sulphur at various pressures were measured thermoelectrically:

Pressure.	Boiling point.	Pressure.	Boiling point.
1.35 mm.	210.2°	20.5 mm.	265.0°
3.20 „	222.4	53.5 „	306.5
5.54 „	234.4	133.0 „	352.5
8.45 „	241.8	250.1 „	379.4

When the pressure exceeds 4 mm., it is found that the boiling point of sulphur is independent of the intensity of the heating.

T. H. P.

Isomorphism of Selenium and Tellurium. GIOVANNI PELLINI and GIOVANNI VIO (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 46—53. Compare this vol., ii, 609, and Ringer, *Abstr.*, 1902, ii, 651).—The

authors have determined the solidifying points of mixtures of carefully purified selenium and tellurium in varying proportions, the results being given in tables and in the form of a curve. The solidifying points of all the mixtures lie between those of the components. The upper portions of the solidified mixtures are richer in selenium than the lower ones. All the mixtures solidify in mixed crystals of the hexagonal-rhombohedral type, which is that to which the crystals of both selenium and tellurium belong. The isomorphism of these two elements is hence confirmed. T. H. P.

Combination of Ammonia with Aurous Chloride, Bromide, and Iodide. FERNAND MEYER (*Compt. rend.*, 1906, 143, 280—282).—The compound, $\text{AuI}, 6\text{NH}_3$, obtained in the form of white crystals or as an amorphous powder by the action of either liquid or gaseous ammonia on aurous iodide (Abstr., 1905, ii, 42), has a dissociation pressure equal to 760 mm. at 28° and loses 5NH_3 when heated from -28° to $+20^\circ$; the residual compound, AuI, NH_3 , is a fine white powder, stable at the ordinary temperature, but breaks down on heating into ammonia, iodine, and gold; it is also decomposed by water with the formation of ammonium iodide and gold, or by dilute acids yielding the ammonium salt of the acid and aurous iodide.

The compound $\text{AuBr}, 2\text{NH}_3$, obtained by the action of dry ammonia on aurous bromide at 18° , forms a fine white powder with properties similar to those of the compound AuI, NH_3 .

The compound $\text{AuCl}, 12\text{NH}_3$, obtained by the action of liquid ammonia on aurous chloride, is stable at -28° under atmospheric pressure, but loses 9NH_3 when the temperature is raised to $+20^\circ$, forming the compound $\text{AuCl}, 3\text{NH}_3$, which is stable at 180° , but decomposes at a higher temperature into ammonium chloride and gold.

M. A. W.

Crystallography of Certain Double Salts of Hydrazine. FRANCESCO RANFALDI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 95—101).— $\text{CuCl}_2, 2\text{N}_2\text{H}_5\text{Cl}, 2\text{H}_2\text{O}$ melts and decomposes at $87-88^\circ$ and forms azure-blue, monoclinic crystals [$a : b : c = 1.26546 : 1 : 1.85623$; $\beta = 67^\circ 17' 49''$].

$\text{CuCl}_2, 2\text{N}_2\text{H}_5\text{Cl}, \frac{1}{2}\text{H}_2\text{O}$ melts and decomposes at $149-150^\circ$ and forms green, rhombic crystals [$a : b : c = 1.20272 : 1 : 2.53515$].

$3\text{CuBr}, \text{N}_2\text{H}_5\text{Br}, \text{N}_2\text{H}_5\text{Cl}$ forms colourless, shining, tetragonal crystals [$c = 1.71244$] melting at $145-147^\circ$. T. H. P.

Hydrogen Phosphide Poisoning by Ferrosilicon. P. LEHNKERING (*Zeit. Nahr. Genussm.*, 1906, 12, 132—135).—A sample of electrolytic ferrosilicon ($\text{Si} = 57.69$ per cent.) yielded, in presence of water, 0.00227 per cent. of hydrogen phosphide, whilst the water was found to contain calcium hydroxide amounting to 0.00476 per cent. of the ferrosilicon. The total phosphorus was 0.15 per cent., and is derived from the iron or from the coke.

Four fatal cases of poisoning by hydrogen phosphide have occurred on Rhine boats carrying ferrosilicon, and two explosions in Liverpool in 1904 are attributed to production of hydrogen phosphide.

N. H. J. M.

Synthesis of the Sulphur Compounds of Arsenic: Melting Point and Transformation Curves of these Compounds. W. BORODOWSKI (*Chem. Centr.*, 1906, ii, 297; from *Sitzungsber. Naturf.-Ges. Dorpat.*, 14, 159—180).—The methods employed by the author for the preparation of arsenic-sulphur compounds were: (1) fusion of the mixed components; (2) crystallisation of the product from aqueous solutions of the alkali hydroxides or carbonates; (3) double decomposition of arsenious or arsenic oxide with hydrogen sulphide or carbon disulphide. Method (1) yields no individual compound; by method (2) or (3), realgar and dimorphin, As_2S_3 , can be obtained. Orpiment can only be prepared by double decomposition, by which method, however, As_2S_5 could not be obtained.

The diagram constructed from the melting points and transition temperatures of mixtures of arsenic and sulphur shows that orpiment and realgar exhibit distectic points, but that dimorphin is not a chemical compound. It is further found that orpiment occurs in two modifications, the yellow or β -form, stable at low temperatures, being converted at 170° into a red or α -form, melting at 300° . Realgar also exists in two modifications, the stable red or α -form, with sp. gr. 3.506 at 19° , being transformed at 267° into a black β -form, which has sp. gr. 3.254 at 19° , melting point 307° , and boiling point 565° under 760 mm. pressure. β -Realgar forms a discontinuous series of mixed crystals with arsenic. Mixed crystals are also apparently formed with orpiment and sulphur. T. H. P.

Investigation of Silicate-fusions. CORNELIO DOELTER (*Monatsh.*, 1906, 27, 433—464. Compare this vol., ii, 350).—The melting points of silicates are determined best by the optical method by means of the crystallisation microscope for high temperatures; only in the case of simple silicates are equally accurate results obtained by the electrical method. The simple silicates are only slightly viscous when fused, melt within small temperature intervals, 10 — 30° , and crystallise readily, whereas complicated silicates which when heated decompose into two components, have high viscosities, melt only within larger temperature intervals, 60 — 100° , and have little tendency towards crystallisation. The work of Day and Allen (this vol., ii, 177) is criticised; the artificial feldspars prepared by these authors are not necessarily identical with the natural minerals.

Curves are given showing the changes which take place in the viscosities of fused labradorite, orthoclase, alumina-augite, and elæolite as the temperature falls. These silicates, which remain mobile when cooled below their temperatures of fusion, crystallise readily and are mostly not decomposed when heated.

The temperatures of fusion of mixtures of crystalline silicates, of softening of the corresponding glasses, and of solidification of the fused mixtures are determined and the resulting curves compared. The temperature of solidification is found to depend closely on the extent of the super-cooling. The interval between the temperatures of fusion and of solidification of eutectic mixtures diminishes with the viscosity.

A number of observations point to dissociation of fused silicates.

G. Y.

Mutual Relationship of Potassium and Sodium Sulphates.

JACOBUS H. VAN'T HOFF and HERMANN BARSCHALL (*Zeit. physikal. Chem.*, 1906, **56**, 212—214).—After examination of the experimental evidence, the authors adhere to the view expressed previously that glaserite is not a definite compound, but merely corresponds with the maximum point in a series of isomorphous mixtures of sodium and potassium sulphates. J. C. P.

Alloys of Sodium with Lead, Cadmium, Bismuth, and Antimony. C. H. MATHEWSON (*Zeit. anorg. Chem.*, 1906, **50**, 171—198. Compare this vol., ii, 165; Heycock and Neville, *Trans.*, 1889, **55**, 668; 1892, **61**, 888; Kurnakoff, *Abstr.*, 1900, ii, 277).—From an investigation of these systems by Tammann's method of thermal analysis, controlled, when possible, by microscopic observations, evidence has been obtained of the existence of the following series of compounds: Na_4Pb , Na_2Pb , NaPb , Na_2Pb_5 ; NaCd_2 , NaCd_5 ; Na_3Bi , NaBi ; Na_3Sb , NaSb .

Sodium-lead Alloys.—The freezing-point curve shows four maxima at 386° and 80 atom. per cent., 405° and 66.7 atom. per cent., 367° and 50 atom. per cent., and 319° and 27.4 atom. per cent. of sodium, corresponding with the compounds Na_4Pb , Na_2Pb , NaPb , and Na_2Pb_5 , and four eutectic points at 373° and 76 atom. per cent., 329° and 58.5 atom. per cent., 301° and 37.3 atom. per cent., and 307° and 21.1 atom. per cent. of sodium respectively. The compounds Na_2Pb and Na_4Pb form with one another two series of mixed crystals; the limit of saturation with respect to Na_2Pb lies at 78.5 atom. per cent., that with respect to Na_4Pb at 70 per cent. of sodium. A third series of mixed crystals separates from alloys containing 0—4.1 atom. per cent. of sodium.

The alloy consisting of the compound Na_4Pb can readily be crushed with the fingers and is light grey in colour; the compound Na_2Pb is light blue and very brittle. The compounds NaPb and Na_2Pb_5 are about as hard as calcite, the other two are considerably softer.

Sodium-cadmium Alloys.—The freezing-point curve of this system has two maxima at 385° and 33.3 atom. per cent. and 360° and 16.2 atom. per cent. sodium, corresponding with the compound NaCd_2 and NaCd_5 respectively, as well as three eutectic points at 95° and 99.2 atom. per cent., 346° and 21 atom. per cent., and 285° and 5.6 atom. per cent. of sodium respectively. Further, owing to the limited mutual solubility of the compound Na_2Cd and sodium, and the consequent separation into two liquid layers, the curve is horizontal between 60 and 70 atom. per cent. of sodium.

The compounds NaCd_5 and NaCd_2 have the same colour as their components and are brittle; they are harder than cadmium and are not affected by absolute alcohol.

Sodium-bismuth Alloys.—The freezing-point curve shows a maximum at 775° and 75 atom. per cent. sodium, corresponding with the composition of the compound Na_3Bi , a eutectic point at 218° and 22 atom. per cent. sodium, and a break at 445° and 47 atom. per cent. of the same metal. It is shown by thermal analysis that the latter point is due to the existence of a second compound, NaBi , which decomposes below its melting point.

The compound Na_3Bi is bluish-violet in colour, brittle, and becomes rapidly oxidised in moist air; NaBi is less brittle, and both compounds have about the same degree of hardness as bismuth.

Sodium-antimony Alloys.—The freezing-point curve shows two maxima at 856° and 75 atom. per cent. and 465° and 50 atom. per cent. of sodium respectively, corresponding with the compounds Na_3Sb and NaSb , and two eutectic points at 435° and 55.5 atom. per cent. and 400° and 39.4 atom. per cent. of sodium respectively.

The compound NaSb has the same colour as metallic antimony, whilst Na_3Sb , which is harder and more easily oxidised, is deep blue.

The paper concludes with a discussion of the rules governing the combining capacity of sodium for other elements. G. S.

Silver Sulphide, Selenide, and Telluride. HENRI PÉLABON (*Compt. rend.*, 1906, 143, 294—296).—The author has determined the freezing-point curves for mixtures of silver with sulphur, selenium, or tellurium. In the case of sulphur, a mixture could not be obtained richer in sulphur than the sulphide Ag_2S , which melts at 825° ; the eutectic mixture melts at 800° . Mixtures of silver and selenium containing from 5 to 60 per cent. of silver separate at 620° into two layers, the upper consisting of pure selenium, the lower of a mixture of silver and selenium in atomic proportions; as the proportion of silver is increased the solidifying points rise to 880° , the melting point of the selenide Ag_2Se ; the eutectic mixture melts at 830° and contains 80.5 per cent. of silver.

The freezing-point curve of mixtures of silver and tellurium shows two eutectics melting at 345° and 825° , containing respectively about 34 and 78 per cent. of silver, and a maximum at 955° corresponding with the telluride Ag_2Te . M. A. W.

Alloys of Silver with Thallium, Bismuth, and Antimony. G. I. PETRENKO (*Zeit. anorg. Chem.*, 1906, 50, 133—144).—From an investigation of these systems by Tammann's method of thermal analysis, controlled by microscopic observations, the author draws the conclusion that only antimony and silver enter into chemical combination with formation of a compound Ag_3Sb .

Silver-thallium Alloys (compare Heycock and Neville, *Trans.*, 1894, 65, 31; *Abstr.*, 1897, ii, 245).—The freezing-point curve of this system consists of two branches which meet in a eutectic point at 287° ; the eutectic mixture contains 2.5 per cent. by weight of silver. The melting point of thallium is 303 — 304° . The elements form only one series of mixed crystals, which contain 0—10 per cent. by weight of thallium.

Silver-bismuth Alloys (compare Laurie, *Trans.*, 1894, 65, 1031; Heycock and Neville, *Abstr.*, 1897, ii, 245).—The freezing-point curve in this case also consists of two branches which meet in a eutectic point at 262° ; the eutectic mixture contains 2.5 per cent. by weight of silver. An unusual feature of the curve is that the larger branch is concave upwards. The elements form only one series of mixed crystals, containing 0—5 per cent. by weight of bismuth.

Silver-antimony Alloys (compare Gautier, *Abstr.*, 1896, ii, 646;

Heycock and Neville, Abstr., 1897, ii, 245).—The freezing-point curve of the system consists of three branches: it has a break at 560° and 27.07 per cent. by weight of antimony, corresponding with the composition of the compound Ag_3Sb , and a eutectic point at 485° and 45 per cent. by weight of antimony. From alloys containing 0—15 per cent. by weight of the latter element, a series of mixed crystals separates; at the latter point they are saturated. G. S.

Reciprocal Transformation of Calcium Monoborates. JACOBUS H. VAN'T HOFF and U. BEHN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1906, 38, 653—656).—It was observed in the preparation of calcium borate that there was some uncertainty in the preparation of a homogeneous crystalline material. More minute investigation showed that besides the hexahydrate, $\text{CaB}_2\text{O}_4 \cdot 6\text{H}_2\text{O}$, a tetrahydrate, $\text{CaB}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$, existed. The temperature of transformation, determined with the aid of the dilatometer, appeared to be 45.5° , but estimations of the electrical conductivities indicated another value. In order to avoid the disturbing influence of the carbon dioxide of the atmosphere, the determinations had to be carried out in a special apparatus, a detailed description of which is given. It was thus found that the temperature of transformation of the hexa- into the tetra-hydrate was about 23° . It is suggested that the value found by the dilatometer is probably the transition point of the hexa-hydrate and dihydrate. K. J. P. O.

Strontium Amalgams. ANTOINE GUNTZ and G. ROEDERER (*Bull. Soc. chim.*, 1906, [iii], 35, 494—503).—When an aqueous solution of strontium chloride is decomposed electrolytically, using a mercury electrode in the manner suggested by Feré (Abstr., 1899, ii, 155), two strontium amalgams are formed: the one liquid and the other crystalline. The latter has the formula SrHg_{11} , and is identical with that already described by Guntz and Feré (Abstr., 1896, ii, 421; 1902, ii, 138). The authors do not accept the statement of Kerp and Böttger (Abstr., 1900, ii, 656), that this amalgam is merely a mixture of their amalgam SrHg_{12} with a decomposition product, and on the contrary state that they have never been able to observe the formation of the amalgam to which Kerp attributes the formula SrHg_{12} . The amalgam SrHg_{11} remains unchanged when centrifugated or when submitted to a pressure of 5000 kilos. per sq. cm. in an atmosphere of carbon dioxide. By heating the crystalline amalgam under special conditions, described in detail in the original, products richer in strontium can be obtained. One of these has approximately the composition represented by the formula Sr_2Hg_5 . Another, which is silver-white, distinctly crystalline, with a hardness between 2 and 3, is probably represented by the formula SrHg_6 . The richest amalgam obtainable in this way contains 52 per cent. of strontium. When the heating is continued beyond this stage, the amalgam begins to distil, and consequently it is impossible in this way to prepare metallic strontium from the pure amalgam. If, however, the amalgam initially contains strontium hydride, the latter will dissociate on heating, and under such circumstances the distillate will contain metallic strontium.

T. A. H.

Preparation of Pure Barium from its Suboxide. ANTOINE GUNTZ (*Compt. rend.*, 1906, 143, 339—340).—When a mixture of equivalent quantities of barium oxide with magnesium or barium is heated in a vacuum at 1100° , *barium suboxide*, Ba_2O , is formed, which decomposes water, absorbs nitrogen at a red heat to form the nitride, Ba_3N_2 , and hydrogen to form the hydride, BaH_2 . Barium suboxide dissociates at high temperatures, and if a mixture of barium oxide and magnesium in the proportion of $3\text{BaO} : \text{Mg}$ is heated at 1100° , an alloy of barium and magnesium containing 37 per cent. of barium distils from the mass and can be condensed in a cooled steel tube; if, however, the magnesium in the above reaction is replaced by a non-volatile metal, it is possible to obtain pure barium by this method of reduction, thus a crystalline metal containing 98.8 per cent. of barium was obtained by heating a mixture of barium oxide with one-tenth its weight of aluminium at 1200° ; metallic strontium can be prepared similarly. M. A. W.

Mixed Crystals of Barium Chloride and Bromide. JEAN HERBETTE (*Compt. rend.*, 1906, 143, 243—245).—A solution containing barium chloride and bromide deposits mixed monoclinic crystals which may have: (1) the form of the chloride, (2) the form of the bromide, or (3) an intermediate form, for which, when the crystals contain about 50 per cent. of the bromide, $a : b : c = 1.7104 : 1 : 1.6240$ and $\beta = 89^{\circ}50'5''$. All the crystals have the composition $\text{BaCl}_n\text{Br}_{2n}, 2\text{H}_2\text{O}$. There appears to be no gap in the variation of chemical composition between the chloride and the intermediate crystals, although one exists between the intermediate form and the bromide. T. H. P.

Solubility of Barium Sulphate in Hydrogen Peroxide. A. GAWALOWSKI (*Chem. Centr.*, 1906, ii, 7—8; from *Zeit. Oesterr. Apoth.-Ver.*, 44, 258).—Barium sulphate exhibits considerable solubility in hydrogen peroxide solutions. T. H. P.

Borostannates of the Alkaline Earths; Reproduction of Nordenskiöldite. LÉON OUVRARD (*Compt. rend.*, 1906, 143, 315—317).—Crystals of calcium borostannate, $\text{CaO}, \text{B}_2\text{O}_3, \text{SnO}_2$, slightly contaminated with stannic oxide, are obtained when a mixture of precipitated calcium borate and pure stannic oxide is heated to whiteness in a platinum boat in a current of hydrogen chloride; better formed crystals of the pure compound can be prepared by passing a mixture of air and stannic chloride vapour over calcium borate heated to redness. Calcium borostannate thus prepared forms colourless, transparent, rhombohedral crystals, flattened at the base, 1.2 mm. long and 0.01 mm. thick; their crystallographic properties have been examined by Schulten, and they are found to be identical with the natural compound, nordenskiöldite (Brögger, *Abstr.*, 1890, 1078); they have a sp. gr. 4.8 at 15° , slightly higher than that of the mineral (4.2), which, however, always contains a little zirconia and traces of volatile impurities. Crystalline borostannate of strontium or barium can be prepared similarly. M. A. W.

Basic Carbonates. WILLIAM A. DAVIS (*J. Soc. Chem. Ind.*, 1906, 25, 788—798. Compare Anderson, *Trans.*, 1905, 87, 257; Brill, *Abstr.*, 1905, ii, 522).—Magnesium carbonate is soluble to a considerable extent in water containing excess of carbon dioxide, but when the pressure of the latter falls sufficiently, a salt having the empirical formula $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ separates in colourless crystals. It has usually been considered that the magnesium hydrogen carbonate present in such solutions loses carbon dioxide on evaporation or by diffusion, the normal carbonate being precipitated, but the author finds that the crystalline trihydrate loses 2 mols. of water when heated in a current of air at 100° , whilst the remaining molecule is only driven off at a much higher temperature with partial decomposition, and he therefore regards the trihydrate as a hydrated hydroxy-carbonate having the constitution $\text{OH} \cdot \text{Mg} \cdot \text{CO}_3 \text{H} \cdot 2\text{H}_2\text{O}$. When, therefore, the solution of the bicarbonate is allowed to stand, or is heated at a temperature not exceeding 80° , it reacts with water according to the equation $\text{Mg}(\text{CO}_3\text{H})_2 + \text{H}_2\text{O} = \text{OH} \cdot \text{Mg} \cdot \text{CO}_3\text{H} + \text{H}_2\text{CO}_3$.

When the compound $\text{OH} \cdot \text{Mg} \cdot \text{CO}_3\text{H} \cdot 2\text{H}_2\text{O}$ is heated with boiling water, two reactions take place simultaneously according to the equations $\text{OH} \cdot \text{Mg} \cdot \text{CO}_3\text{H} \cdot 2\text{H}_2\text{O} = \text{OH} \cdot \text{Mg} \cdot \text{CO}_3\text{H} + 2\text{H}_2\text{O}$; $\text{OH} \cdot \text{Mg} \cdot \text{CO}_3\text{H} + \text{H}_2\text{O} = \text{Mg}(\text{OH})_2 + \text{H}_2\text{O} + \text{CO}_2$, the product thus consisting of a mixture of magnesium hydroxide and hydroxy-carbonate.

Reference is also made to the existence of double carbonates of magnesium and the alkali metals, for example, $\text{MgCO}_3 \cdot \text{Na}_2\text{CO}_3$ or $\text{Mg}(\text{CO}_3\text{Na})_2$ (Deville, 1851; Reynolds, *Trans.*, 1898, 73, 262). An important characteristic of these mixed salts is their considerable solubility in water; thus, when sodium hydroxide is added to a solution of magnesium hydrogen carbonate, no solid separates until the temperature is raised sufficiently to decompose the double salt.

The basic carbonates of magnesium of commercial importance are generally prepared by interaction of magnesium sulphate and sodium carbonate in aqueous solution. It has often been supposed that in this reaction the normal carbonate is first formed and part of it is subsequently hydrolysed to hydroxide, but the author, on the basis of the observations referred to above, suggests an alternative view; he considers that the primary reaction proceeds according to the equation $2\text{Na}_2\text{CO}_3 + \text{MgSO}_4 = \text{Mg}(\text{CO}_3\text{Na})_2 + \text{Na}_2\text{SO}_4$, the double carbonate subsequently undergoing hydrolysis with formation of a mixture of hydroxy-carbonate and hydroxide. Further, when the precipitate first produced is allowed to remain in contact with the mother liquor, it changes to crystalline magnesium hydroxy-carbonate, $\text{OH} \cdot \text{Mg} \cdot \text{CO}_3\text{H} \cdot 2\text{H}_2\text{O}$. Commercial basic carbonates of magnesium ("magnesia alba") thus consist of a mixture of the three compounds, $\text{OH} \cdot \text{Mg} \cdot \text{CO}_3\text{H} \cdot 2\text{H}_2\text{O}$, $\text{OH} \cdot \text{Mg} \cdot \text{CO}_3\text{H}$, and $\text{Mg}(\text{OH})_2$, in proportions depending on the method of preparation. As a matter of fact, commercial samples contain 1—4 mols. of the carbonate to 1 of the hydroxide, and microscopic observation indicates their heterogeneous character.

These views receive practical application in the softening of waters containing magnesium carbonate, and in the Solvay process of manufacturing potassium carbonate with the aid of magnesia. In the former case the waters cannot be softened by addition of sodium

hydroxide unless the temperature is raised sufficiently to decompose the double salt first formed.

The hydroxy-carbonate is soluble not only in alkali carbonate, but to some extent in solutions of other salts, such as magnesium sulphate, and it is probable that in these cases also double salts are present in solution.

The paper is illustrated by eight micro-photographs.

G. S.

Zinc and Arsenic. K. FRIEDRICH and A. LEROUX (*Metallurgie*, 1906, 3, 477—479).—The freezing-point curve has been determined for alloys containing from 0 to 14 per cent. of arsenic. The curve rises directly from the freezing point of zinc, and a maximum does not occur within the limits studied. The horizontal line at 419° is unbroken. Microscopic examination shows white crystals, which may be either a compound or a solid solution of zinc and arsenic in a ground-mass of zinc.

C. H. D.

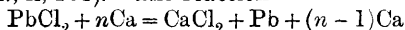
Behaviour of Zinc Oxide at High Temperatures. F. O. DOELTZ [and C. A. GRAUMANN] (*Metallurgie*, 1906, 3, 212—216, 233—238).—When pure zinc oxide is heated in an electric furnace in a current of air free from reducing substances, no appreciable loss of weight is observed at 1000° . The loss becomes appreciable at 1100° and increases with rise of temperature, until at 1400° it may amount to 13 per cent. in two hours. When strewn on a platinum wire heated electrically nearly to 1700° , zinc oxide volatilises rapidly. Micro-photographs are given, showing the formation of well-developed crystals of zinc oxide during volatilisation.

C. H. D.

Behaviour of Cadmium Oxide at High Temperatures. F. O. DOELTZ and C. A. GRAUMANN (*Metallurgie*, 1906, 3, 372—375).—The experiments were carried out in the manner adopted for zinc oxide (see preceding abstract). Cadmium oxide volatilises appreciably at 800° , rapidly at 1000° .

C. H. D.

Alloys of Lead and Calcium. L. HACKSPILL (*Compt. rend.*, 1906, 143, 227—229).—The author has prepared alloys of lead and calcium by reducing lead chloride by means of excess of calcium (compare this vol., ii, 161). The reaction



disengages 85.9 cals. without taking account of the heat furnished by the formation of the alloy of lead and calcium; when small pieces of calcium are thrown into fused lead chloride, an explosive reaction occurs. This method cannot be employed for the preparation of alloys containing more than about 27 per cent. of calcium. The alloys obtained are harder and less malleable than lead, and their section is bright, but rapidly tarnishes in the air. On heating the alloys in the air, the calcium is first attacked, yielding lime and calcium nitride, which partially protect the lead against oxidation. Water attacks them slowly in the cold, and more rapidly on boiling, giving lime and powdered lead.

On removing the excess of lead from these alloys by distillation in a

vacuum, a crystalline alloy is obtained having the composition Pb_3Ca_2 , the melting point 775° , and a sp. gr. 7.6. T. H. P.

Composition of the Copper—Cuprous Oxide Eutectic. E. HEYN (*Rev. de Métallurgie*, 1906, 3, 545—546).—The composition of the copper—cuprous oxide eutectic determined by the author (Abstr., 1904, ii, 406) is confirmed. The value found by Dejean (this vol., ii, 356), namely, 4.5—5.0 per cent. of oxide instead of 3.5 per cent., is too high. It is pointed out that care must be taken in the sampling of these alloys for analysis owing to the friable character of the oxide. C. H. D.

The Nature of Copper Matte. PAUL RÖNTGEN (*Metallurgie*, 1906, 3, 479—487).—The author has determined the freezing-point curve of mixtures of cuprous sulphide and ferrous sulphide. The curve shows three distinct maxima corresponding with the compounds $3\text{Cu}_2\text{S}, 2\text{FeS}$, $\text{Cu}_2\text{S}, \text{FeS}$, and $2\text{Cu}_2\text{S}, 5\text{FeS}$, melting at 1060° , 1030° , and 980° respectively. The form of the curve between 35 and 55 per cent. of ferrous sulphide is uncertain, and the existence of a fourth compound, $2\text{Cu}_2\text{S}, 3\text{FeS}$, is possible, but has not been proved. The microscopic examination of the polished and etched sections indicates that important changes, which, however, have not been more fully investigated, take place below the solidifying points of the sulphide compounds. A partial separation of metallic copper is often observed during the fusion, reaching its maximum in the mixture containing 25 per cent. of ferrous sulphide. This appears to be due to the removal of sulphur from cuprous sulphide by a portion of the ferrous sulphide, the compound $\text{Cu}_2\text{S}, 2\text{FeS}$ being decomposed, yielding FeS_2 and metallic copper. The occurrence of native copper in mineral deposits containing the sulphides is perhaps due to this reaction. C. H. D.

Oxides of Thallium. II. OTTO RABE (*Zeit. anorg. Chem.*, 1906, 50, 158—170. Compare this vol., ii, 285).—Werther (1864) and Heiberg (Abstr., 1903, ii, 614) have observed that when thallic oxide is kept at 100° , or even at 60 — 70° , in an ordinary drying oven heated by a Bunsen burner it continues to gain in weight, and simultaneously undergoes reduction to the thallous state. They were of opinion that the increase of weight is due to the formation of thallous carbonate and sulphate, the sulphur coming from the gases given off by the burner. The author has repeated these experiments with the ordinary oxide and with the black oxide described in the former paper, and confirms their results as far as the gradual increase in weight is concerned. It is shown, however, that no carbonate is formed, but a mixture of normal and acid thallous sulphates. The reduction is comparatively slow at 65° , but at 115° the brown oxide is completely transformed into a mixture of the two sulphates in 468 hours. The black oxide is similarly, but much more slowly, acted on. When the oxides are heated under such conditions that the gases from the burner cannot reach them, the weight remains constant. G. S.

Antimony-thallium Alloys. ROBERT S. WILLIAMS (*Zeit. anorg. Chem.*, 1906, 50, 127—132).—In agreement with Levin (Abstr., 1905, ii, 462) the author finds that thallium exists in two modifications, the β -changing into the α -form when the temperature falls below 225°.

Thallium and antimony are miscible in all proportions. The freezing-point curve of the system consists of two branches, which meet in a eutectic point at 29.8 atom. per cent. of antimony; the eutectic temperature is 195°. From alloys containing 0—22 atom. per cent. of antimony (which solidify above 225°) β -thallium separates out first, whilst with from 22—29.8 per cent. of the former metal mixed crystals of α -thallium and antimony separate. These results are in accord with the fact that the transition temperature of thallium is not affected by the presence of antimony, so that the latter element appears to be insoluble in β -thallium. When the temperature of the solid alloy falls to 187°, 8° below the eutectic point, the components interact with formation of a compound which, as shown by thermal analysis, has probably the formula SbTl_3 . The reaction is, however, only partial; when the components, in the proportions required by the formula, have been heated for fifteen hours at 177°, crystals of antimony can still be observed.

Alloys containing less than 50 atom. per cent. of thallium are hard and brittle, but become softer as the amount of this element is further increased. G. S.

Constitution of Amalgams. GEORGE MCPHAIL SMITH (*Amer. Chem. J.*, 1906, 36, 124—135).—A *résumé* of the views of previous authors on the constitution of amalgams. The degree of accuracy of the methods employed in determining molecular weights allows of the determination of n but not of m in the general formula M_nHg_m . The liquid amalgams of the alkali and the alkaline earth metals are solutions in mercury of compounds of the general formula MHg_m . Other metals, such as zinc, cadmium, bismuth, lead, and tin, dissolve in, but do not form compounds with, mercury. G. Y.

Sodium and Barium Mercuric Iodides. ANDRÉ G. DUBOIN (*Compt. rend.*, 1906, 143, 313—314).—Sodium mercuric iodide, $2\text{NaI}, \text{HgI}_2, 4\text{H}_2\text{O}$, obtained in the form of flattened crystals from the heavy saturated solution of the salt (Abstr., 1905, ii, 637) by prolonged evaporation in dry air, is very deliquescent, has a sp. gr. of about 3 at 0°, and differs from the salt $2\text{NaI}, \text{HgI}_2$, similarly obtained by Boullay (*Ann. Chim. phys.*, 1827, 34, 350). Barium mercuric iodide, $\text{BaI}_2, \text{HgI}_2, 5\text{H}_2\text{O}$, forms very large, flattened crystals, 1 to 2 mm. thick and 2 cm. long, and has a sp. gr. of about 4 at 0°. M. A. W.

Yttrium Chloride. CAMILLE MATIGNON (*Ann. Chim. phys.*, 1906, [viii], 8, 433—439. Compare Abstr., 1905, ii, 391, 458; this vol., ii, 169).—Hydrated yttrium chloride, $\text{YtCl}_3, 6\text{H}_2\text{O}$, prepared by the action of a concentrated solution of hydrogen chloride on the oxide, occurs in deliquescent prisms and melts at 156—160°. By dehydration in a current of hydrogen chloride, the anhydrous chloride is obtained. The latter fuses at a lower temperature than do the chlorides of lanthanum

and certain other rare earths, and does not change colour on heating. It has a sp. gr. 2.8 at 18°, and its molecular heat of solution is 45.4 Cal. Its molecular weight in absolute alcohol, as determined by the boiling-point method, is 172, the theoretical value being 195. One hundred grams of absolute alcohol dissolve 60.1 grams of the anhydrous salt at 15°, and it also forms additive compounds with this solvent, the best defined one having the formula $\text{YtCl}_3 \cdot \text{C}_2\text{H}_6\text{O}$. One hundred grams of pyridine dissolve 6.5 grams of the salt, and in this case also additive compounds are formed. The anhydrous salt is also slightly soluble in quinoline.

The values of the physical constants thus obtained are compared with those previously observed for the chlorides of samarium and neodymium. G. S.

Ytterbium Chloride. CAMILLE MATIGNON (*Ann. Chim. Phys.*, 1906, [viii], 8, 440—443. Compare preceding abstract).—Hydrated ytterbium chloride, $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, obtained by the action of hydrogen chloride solution on the oxide, occurs in colourless, deliquescent crystals and melts at 150—155°. On heating in a current of hydrogen chloride at 110°, a monohydrate, $\text{YbCl}_3 \cdot \text{H}_2\text{O}$, is obtained; at 180—200° the last molecule of water is slowly eliminated. The anhydrous chloride does not fuse quite so readily as the corresponding yttrium compound, and when heated above its melting point readily sublimes. In equivalent concentration it lowers the freezing point of water to the same extent as the other chlorides of the rare earths already examined. G. S.

Cathodic Phosphorescence Spectra of Terbium and Dysprosium diluted with Lime. GEORGES URBAIN (*Compt. rend.*, 1906, 143, 229—231).—By diluting the various pure rare earths with gradually varying proportions of lime, it is found that the optimum of phosphorescence corresponds with mixtures containing from 0.001 to 0.003 gram of rare earth in about 1 gram of pure lime.

On examining in this way the successive terms of a fractionation in a vacuum tube, the phosphorescence spectra observed have about the same sensitiveness as the other spectra, and the agreement of the various spectra (spark, absorption, and phosphorescence) given by the same element is clearly apparent if the fractionation has been carried sufficiently far. This is not the case if observation is limited to the phosphorescence given by the earths either directly or without sufficient addition of lime or other diluent earth, for, in these circumstances, earths such as gadolinia and yttria play the part of diluents.

The earths obtained by the author between gadolinium and yttrium are not directly phosphorescent. They contain terbium, dysprosium, and neo-holmium, and phosphorescence has as yet not been observed in the last named.

When the different fractions were diluted with lime, only two phosphorescence spectra were observed, namely, those of terbium and dysprosium. These are described in detail.

Crookes attributes the citron band ($\lambda = 584.8$) of the dysprosium

spectrum sometimes to an element, G_8 , sometimes to yttrium; de Boisbaudran has shown that the element producing this band is identical with his element Z_a , and the author shows that Z^a is identical with dysprosium.

T. H. P.

Neodymium Chloride. CAMILLE MATIGNON (*Ann. Chim. Phys.*, 1906, [viii], 8, 243—283. Compare this vol., ii, 449).—The author has prepared in a pure state the following compounds of neodymium. Neodymium chloride, $NdCl_3$, and its mono- and hexa-hydrates; $NdCl_3 \cdot 3EtOH$; $NdCl_3 \cdot 3C_2H_5NH_2$; $NdOCl$; $NdBr_3$ and NdI_3 ; $NdH_3(SO_4)_3$ and $(Nd_2O_2)SO_4$.

The trichloride has the following properties: sp. gr. at $18^\circ/4^\circ$, 4.195; melting point, 785° ; sp. gr. of $NdCl_3 \cdot 6H_2O$ at $16.5^\circ/4^\circ$, 2.28; melting point of $NdCl_3 \cdot 6H_2O$, 126° ; 100 grams of water dissolve 98.68 grams of the anhydrous salt at 13° and 140 grams at 100° ; 100 grams of alcohol dissolve 44.50 grams at 20° , and 100 grams of pyridine, 1.8 grams at about 15° . Heat of solution of: (1) Nd_2O_3 in dilute hydrochloric acid, 105.5 Cal.; $NdCl_3 \cdot 6H_2O$ in water, 7.6 Cal.; $NdCl_3$ in water, 35.40 Cal.; $NdCl_3$ in alcohol, 21.5 Cal. Heat of formation of the anhydrous salt, 249.4 Cal.

The action of oxygen below 1000° , or of water vapour, converts the fused chloride into oxychloride, $NdOCl$. The heat of transformation of the chloride into the iodide is expressed by $NdCl_3$ (diss.) + $3HI$ (gas) = NdI_3 (diss.) + $3HCl$ (gas) - 6.6 Cal. The iodide is extremely sensitive to the action of traces of oxygen or moisture. The bromide is apparently isomorphous with the chloride.

T. H. P.

Preparation of Anhydrous Chlorides of Rare Metals.
Praseodymium Chloride. Samarium Chloride. Lanthanum Chloride. CAMILLE MATIGNON (*Ann. Chim. Phys.*, 1906, [viii], 8, 364—416, 426—432).—A detailed account of this work has already been published (*Abstr.*, 1902, ii, 263, 505; 1904, ii, 340, 341; 1905, ii, 165, 391, 458, 525).

M. A. W.

Samarous Chloride. CAMILLE MATIGNON and E. CAZES (*Ann. Chim. Phys.*, 1906, [viii], 8, 417—426).—A *résumé* of work already published (this vol., ii, 169). Samarium iodide is reduced by hydrogen with the formation of *samarous iodide*.

M. A. W.

Preparation of Pure Cerium Compounds. N. A. ORLOFF (*Chem. Zeit.*, 1906, 30, 733).—Advantage is taken of the fact that ceric oxalate, like thorium oxalate, is soluble in ammonium oxalate. The mixture of oxides, dissolved in sulphuric acid, is added to an excess of ammonium oxalate; the precipitate contains lanthanum, neodymium, praseodymium, yttrium, and some cerous oxalate. The filtrate contains thorium and cerium; the cerium slowly precipitates as cerous oxalate, the thorium remaining in solution; the separation of the cerium can be hastened by adding a reducing agent such as sodium sulphite. Salicylic acid also forms a double salt with cerium and can be used as a means of separating pure ceria; but this method is less advantageous.

W. A. D.

Ultramarines. CAMILLE CHABRIÉ and F. LEVALLOIS (*Compt. rend.*, 1906, **143**, 222—224).—On heating ordinary ultramarine with silver nitrate and water in a sealed tube at a constant temperature between 115° and 180°, the products obtained are silver-ultramarine, silver nitrite, sulphuric acid, and nitric oxide.

Ultramarine loses a considerable proportion of its colour when it is heated for 100 hours with water at 200—300°. Sodium sulphide is found in the solution, and the parts which are completely decolorised do not yield hydrogen sulphide when treated with a mineral acid.

After washing with boiling water, a solution of iodine in potassium iodide, and potassium cyanide solution, silver-ultramarine never contains more than 38·47—38·56 per cent. of silver, the complete substitution of sodium by silver requiring 47·95 per cent. of the latter metal. Part of the sodium therefore seems to escape in the transformation of ultramarine into the silver derivative.

Attempts to prepare substituted ultramarines containing ethylene, naphthyl, or triphenylmethyl groups did not lead to definite results.

Ordinary ultramarine is completely freed from sulphur when heated with mercuric oxide.

T. H. P.

Compounds of Manganese and Silicon. FRIEDRICH DOERINCKEL (*Zeit. anorg. Chem.*, 1906, **50**, 117—126. Compare Vigouroux, *Abstr.*, 1896, ii, 249; 1905, ii, 822; Lebeau, *Abstr.*, 1904, ii, 343).—The freezing-point curve of the system shows two maxima at 21·3 and 33·8 per cent. by weight of silicon respectively, corresponding with the composition of the compounds Mn_2Si and $MnSi$, as well as two eutectic points at 1075° and 11 per cent. and 1239° and 30 per cent. by weight of silicon respectively. Between 50 and 100 per cent. by weight of silicon, microscopic observations indicate the presence of a third compound, the crystals of which are characterised by fine parallel markings, but its composition could not be determined by thermal analysis owing to the slight alteration in the melting point of the alloy with change of concentration from 45—50 per cent. silicon. The author is of opinion that the compound in question cannot be $MnSi_2$, which would contain 50·8 per cent. of silicon, whereas crystals of the latter element can be detected in alloys containing only 50 per cent. of silicon. Lebeau (*loc. cit.*), by treating the alloys with various solvents and analysing the residues, has arrived at the conclusion that three compounds of manganese and silicon exist, the respective formulæ of which are Mn_2Si , $MnSi$, and $MnSi_2$. From alloys containing 0—10 per cent. of silicon mixed crystals separate.

The paper is illustrated with six microphotographs.

G. S.

Alloys of Manganese and Molybdenum. ARRIVANT (*Compt. rend.*, 1906, **143**, 285—287).—Alloys of manganese and molybdenum containing 12·25 to 29·64 per cent. of the latter metal, prepared by fusing a mixture of the metallic powders at 1500° in a current of hydrogen, or by reducing a mixture of the oxides by means of aluminium, form hard, brittle, homogeneous ingots, readily soluble in dilute or concentrated mineral acids.

These alloys consist of free manganese associated with one or other of

the compounds Mn_6Mo or Mn_4Mo , which can be separated from the alloy by means of dilute acetic acid or ammonium acetate in dilute alcoholic solution, in which they are insoluble. The compound Mn_6Mo forms brilliant plates, has a sp. gr. 7.28 at 0° , the calculated value being 7.50, and the compound Mn_4Mo forms a bright, granular powder, and has a sp. gr. 7.85 at 0° , the calculated value being 7.62. The compounds are attacked by chlorine or strong mineral acids at the ordinary temperature, by water at 250° , and by the alkali carbonates, nitrates, or hydrogen sulphates at a red heat.

M. A. W.

Washing Colloidal Precipitates. JACQUES DUCLAUX (*Compt. rend.*, 1906, 143, 296—298).—According to Nicolardot (*Abstr.*, 1905, ii, 167) and Wyruboff (*Ann. Chim. Phys.*, 1905, [viii], 7, 449), the compound obtained by prolonged washing of Graham's colloidal ferric hydroxide, $Fe_2(OH)_6, nFe_2Cl_6$, has the composition $Fe_2(OH)_{6, \frac{1}{1.50}}Fe_2Cl_6$, and the amount of chlorine is not diminished by further washing. The author has determined the values of n of the formula $Fe_2(OH)_6, nFe_2Cl_6$, and c , the concentration in mols. per litre of the chlorine in the filtrate obtained in successive washings by dialysis of the colloidal precipitate, and finds that while n diminishes from 0.036 to 0.0022, the values of c fall from 0.006 to 0.000008; the final precipitate, therefore, has the composition $Fe_2(OH)_{6, \frac{1}{1.50}}Fe_2Cl_6$, and the corresponding values of n and c show that the rate of elimination of chlorine from the colloidal precipitate, which is rapid at first, becomes increasingly less rapid, but does not reach a limiting value.

M. A. W.

Copper Steels. PIERRE BREUIL (*Compt. rend.*, 1906, 143, 346—348. Compare this vol., ii, 546).—The author has measured the elasticity, breaking load, and elongation of copper steels tempered at different temperatures; three series of steels were examined, containing 0.15 to 0.18, 0.35 to 0.38, and 0.56 to 0.79 per cent. of carbon respectively, the copper varying in each series from 0.5 to 10 per cent.; the results are tabulated in the original, and show that the increase in the tenacity and diminution in the ductility of the steels effected by the copper varies with the heat treatment the metal has received.

M. A. W.

Reduction of Molybdenum Dioxide by Boron and the Combination of Boron with Molybdenum. ARMAND BINET DU JASSONNEIX (*Compt. rend.*, 1906, 143, 169—172).—Molybdenum cannot be heated in the electric furnace in carbon crucibles without the formation of considerable quantities of crystalline carbides. To avoid this complication, the reduction of molybdenum dioxide by boron has been investigated in magnesia crucibles. The molybdenum-boron alloys obtained in this way are non-crystalline; the density decreases and the hardness increases with the percentage of boron. They are attacked by fluorine in the cold and by chlorine at a red heat, leaving in this case a residue of carbon boride. They are not acted on by solutions of hydrochloric and hydrofluoric acids or by alkalis. Concentrated sulphuric acid acts on warming, and dilute nitric acid dissolves them even in the cold.

Alloys containing more than 46 per cent. of boron could not be prepared in consequence of the formation of boron carbide and of boric acid, which attacks the magnesia crucibles. H. M. D.

Zirconium Silicide, $ZrSi_2$, and Titanium Silicide, $TiSi_2$. OTTO HÖNIGSCHMID (*Compt. rend.*, 1906, 143, 224—226).—By mixing, in a Hessian crucible, 200 grams of powdered aluminium, 250 grams of sulphur, 180 grams of fine sand, and either 15 grams of titanous acid or 40 grams of titanium potassium fluoride (or a corresponding amount of the analogous zirconium compound), then covering the whole with a thin layer of powdered magnesium and igniting by means of a Goldschmidt pastille, the following silicides have been obtained.

Zirconium silicide, $ZrSi_2$, crystallises in small, iron-grey, rhombic columns with a metallic lustre, a hardness approximating to that of felspar, and a sp. gr. of 4.88 at 22°. It is stable in the air, but burns vigorously when its powder is heated on platinum foil. It is not attacked by mineral acids with the exception of hydrofluoric acid, which readily dissolves it, hydrogen being evolved; 10 per cent. potassium or sodium hydroxide solution is without action on it, as also is potassium hydrogen sulphate at a red heat. Fusion with potassium hydroxide decomposes it.

Titanium silicide, $TiSi_2$, crystallises in small, iron-grey, tetragonal pyramids, having a hardness of 4—5 and a sp. gr. 4.02 at 22°. It oxidises with difficulty, but burns in chlorine at below a red heat. It is insoluble in mineral acids excepting hydrofluoric acid, but dissolves slowly in 10 per cent. potassium hydroxide solution. Fused potassium hydroxide reacts vigorously on it at a red heat, but potassium hydrogen sulphate is without action under these conditions. T. H. P.

Preparation of Thorium. HENRI MOISSAN and OTTO HÖNIGSCHMID (*Ann. Chim. Phys.*, 1906, [viii], 8, 182—192).—The authors have attempted to prepare thorium by reducing carefully purified thorium chloride by means of sodium, both in the air and in a vacuum. They were, however, unable to obtain a metal containing less than 3 per cent. of oxide.

Electrolytic processes yielded no better results on account of the unavoidable attacking of the porcelain vessels employed. The appearance of the metal, which is often obtained in definite crystals, indicates that the oxide contained in the bath becomes, in some way, mechanically interposed between the particles of metal at the moment of their deposition.

Preliminary experiments with the electric furnace have led to the fusion of small quantities of the pure metal. T. H. P.

Peroxides of Bismuth. IV. ALEXANDER GUTBIER and R. BÜNZ (*Zeit. anorg. Chem.*, 1906, 50, 210—216. Compare this vol., ii, 174, 234, 551).—In former papers, the authors have shown that when bismuth trioxide is oxidised by chlorine in alkaline solution a mixture of higher oxides is obtained, and they have been unable to isolate any definite chemical compound. Hauser and Vanino (*Abstr.*, 1904, ii, 569) claim to have obtained pure bismuth tetroxide, Bi_2O_4 , by oxidation of

the trioxide with alkaline potassium ferricyanide. The authors have now repeated their experiments and have modified them in some respects, and find that the products resemble in every way those obtained by the use of chlorine; a mixture of oxides is always obtained, which cannot be freed from alkali even by repeated washing, and loses oxygen when dried at 100° . Contrary to the contention of Hauser and Vanino, the oxides have no acidic properties. G. S.

Amicroscopic Gold Nuclei. I. RICHARD ZSIGMONDY (*Zeit. physikal. Chem.*, 1906, **56**, 65—76).—The author has previously expressed the view that ruby glass at the colourless stage contains not only a solution of metallic gold, but also "amicroscopic" particles of gold, that is, ultramicroscopic particles which cannot be detected even in special ultramicroscopical apparatus. While the glass is annealing and becoming coloured, these amicroscopic particles act as centres of crystallisation. This view is supported by the author's more recent experiments with colloidal gold solutions, from which it appears that the fine particles of gold in these act like crystallisation nuclei in supersaturated solutions. Thus the formation of a deep red, transparent, colloidal solution from gold salt and formaldehyde is much accelerated by introducing a little of such a colloidal solution already prepared. J. C. P.

Separation of Silver by Colloidal Gold from Reduction Mixtures containing Silver. II. RICHARD ZSIGMONDY (*Zeit. physikal. Chem.*, 1906, **56**, 77—82. See preceding abstract).—The amicroscopic particles of gold in colloidal gold solutions have the power of acting as crystallisation nuclei for silver in reduction mixtures containing the latter metal. When gold particles are growing in a colloidal gold solution, the liquid is red; when silver particles are growing in a colloidal silver solution, the liquid is yellow. Hence the colour imparted to these solutions by the amicroscopic particles depends not so much on the size of the particles as on the nature of the finely-divided material. J. C. P.

Gold-Bismuth and Gold-Antimony Alloys. RUDOLF VOGEL (*Zeit. anorg. Chem.*, 1906, **50**, 145—157. Compare Heycock and Neville, *Trans.*, 1892, **61**, 888).—From an investigation of these systems by Tammann's method of thermal analysis, controlled by microscopic observations, the conclusion is drawn that only gold and antimony enter into chemical combination, with formation of a compound, AuSb_2 .

The freezing-point curve of the system gold-bismuth consists of two straight branches which meet in a eutectic point at 240° ; the eutectic mixture contains 82 per cent. by weight of bismuth. From 0—4 per cent. by weight of bismuth a series of mixed crystals separates. The alloys of this system are somewhat brittle, and are not harder than their components.

The freezing-point curve of gold-antimony alloys shows a break at 460° and 55 per cent. by weight of antimony, corresponding with the composition of the compound AuSb_2 , and a eutectic point at 360° and 24 per cent. by weight of antimony. No mixed crystals are formed.

The compound AuSb_2 is of the same colour as antimony; it is extremely brittle, and harder than its components.

The paper is illustrated by six microphotographs.

G. S.

Mineralogical Chemistry.

Fluorite Crystals from Nérís-les-Bains. P. CARLES (*J. Pharm. Chim.*, 1906, [vi], 24, 108—110).—The fluorite crystals of Nérís-les-Bains were probably deposited from waters containing alkali hydrogen carbonates and highly charged with carbon dioxide which had passed over beds of fluorite. That water so charged deposits fluorite on gradual loss of carbon dioxide is shown by the following experiment: freshly-precipitated calcium fluoride was supersaturated with carbon dioxide under pressure and filtered after twenty-four hours; the clear filtrate, which was left in a warm place in an open vessel for several days, lost its carbon dioxide and deposited microscopic cubes of fluor spar (compare Abstr., 1901, ii, 506). M. A. W.

Cobaltite from Northern Ontario. JUSTIN S. DE LURY (*Amer. J. Sci.*, 1906, [iv], 21, 275—276).—Cobaltite has been found, for the first time in North America, in Coleman Township in northern Ontario; it occurs with copper-pyrites and iron pyrites in a quartz-vein. The mineral crystallises in cubes and octahedra, or in combinations of these forms, with pitted and striated faces. Analysis gave:

Co.	Fe.	Ni.	As.	S.
29.10	4.55	0.97	44.55	20.73

L. J. S.

Phosphorescent Calcite. WILLIAM P. HEADDEN (*Amer. J. Sci.*, 1906, [iv], 21, 301—308).—Certain specimens of calcite from Joplin, in Missouri, and from Fort Collins, in Colorado, on being exposed to the sun's rays were found to become strongly phosphorescent, and to retain this property, in some cases, for thirteen hours. The phosphorescence can also be excited by the electric spark, by X-rays, or by heating. The crystals from Joplin are yellow, violet, or colourless, but only the yellow portions of the crystals phosphoresce. Analysis of this yellow calcite gave:

SiO ₂ .	CO ₂ .	CaO.	MgO.	MnO.	FeO.	ZnO.
0.032	43.95	55.74	0.113	0.045	0.046	0.014
	Ce ₂ O ₃ .	(Di, Sm, La) ₂ O ₃ .	(Yt, Er) ₂ O ₃ .	Total.		
	0.007	0.012	0.013	99.975		

Also traces of SO₃, P₂O₅, Cl, SrO, Al₂O₃, Cr₂O₃, NH₃, and Na₂O, but no sulphides or organic matter.

Some specimens of the non-phosphorescent calcite contained still larger amounts of rare earths, but relatively less of the yttrium group; it is therefore believed that the phosphorescence is connected with the presence of some member of the yttrium group. The spectrum of light which has traversed the violet calcite exhibits the absorption bands of didymium.

L. J. S.

Stibiotantalite. SAMUEL L. PENFIELD and W. E. FORD (*Amer. J. Sci.*, 1906, [iv], 22, 61—77).—This rare mineral, previously known only as rolled pebbles in tin-gravels from Western Australia (Trans., 1893, 63, 1076), has recently been found in well-crystallised specimens at the tourmaline locality at Mesa Grande, San Diego Co., California, where it is associated with tourmaline, pink beryl, quartz, orthoclase, lepidolite, and rarely cassiterite. The crystals are orthorhombic, and resemble columbite in general habit and axial ratios [$a:b:c = 0.7995:1.08448$], and they likewise possess a distinct cleavage parallel to the macropinacoid. They are hemimorphic, but this lower degree of symmetry is usually obscured by polysynthetic twinning, which is complex and invariably present, although often only revealed by the pyroelectric character of the crystals. The mineral is usually of a rich brown colour with a resinous to adamantine lustre, and cleavage fragments closely resemble blende in appearance. The optical constants vary with the chemical composition; the refractive indices and double refraction are unusually high (γ for yellow light being 2.4568 and 2.4588 in two specimens, which are higher than for diamond). Analyses of two crystals gave the following results (in which the relative amounts of tantalic and niobic acids were calculated from the sp. gr. of the precipitated mixed oxides):

Ta_2O_5 .	Cb_2O_5 .	Sb_2O_3 .	Bi_2O_3 .	Total.	Sp. gr.
36.35	18.98	44.26	0.33	99.92	6.72
11.16	39.14	49.28	0.53	100.11	5.98

These analyses give the ratio $Sb_2O_3 : (Ta,Cb)_2O_5 = 1:1$, with a little bismuth replacing antimony. The formula may be written as an antimony salt of normal tantalic and columbic acids, $Sb(Ta,Cb)O_4$, or, having regard to the crystallographic relationship between stibiotantalite and columbite, as an antimony salt, $(SbO)_2(Ta,Cb)_2O_6$, corresponding with columbite, $Fe(Ta,Cb)_2O_6$. The mineral is readily soluble in hydrofluoric acid, but insoluble in other acids. From its solution hydrogen sulphide precipitates antimony trisulphide, proving the antimony to be trivalent and not quinquevalent. Curves expressing the relation between the composition and sp. gr. indicate that the end members, $(SbO)_2Ta_2O_6$ and $(SbO)_2Cb_2O_6$, of the series would have sp. gr. 7.90 and 5.73 respectively. The majority of the crystals have sp. gr. 6.6 to 6.7.

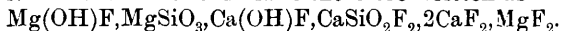
L. J. S.

Silicomagnesiofluorite, a New Mineral from Finland. PETR A. ZEMJATSCHEVSKY (*Zeit. Kryst. Min.*, 1906, 42, 209—213).—The new mineral was found at Luppiko, near Pitkäranta, and is associated with serpentine and quartz. It forms radially-fibrous, hemispherical aggregates, and has an ash-grey, green or blue colour with a

silky lustre. The hardness is 2·5, the sp. gr. 2·91, and the melting point 962°. The fibres are optically positive with weak birefringence and extinguish parallel to their length. The mineral is readily soluble in acids, effervescing in sulphuric acid. Analysis gave:

SiO ₂ .	CaO.	MgO.	Fe ₂ O ₃ .	Mn ₂ O ₄ .	SO ₃ .	H ₂ O.	F.
19·86	38·48	18·27	2·30	0·06	0·27	5·89	31·01

This gives the empirical formula $\text{H}_2\text{Ca}_4\text{Mg}_3\text{Si}_2\text{O}_7\text{F}_{10}$. The water is lost only at a high temperature; the loss of 0·78 per cent. at 300—400° partly represents organic matter. The mineral contains Ca : Mg in the ratio of 4 : 3, whilst nitric acid extracts these elements in the ratio of 2 : 1. The formula is therefore written as



L. J. S.

Two Pseudomorphs from Canada. RICHARD P. D. GRAHAM (*Amer. J. Sci.*, 1906, [iv], 22, 47—54).—Orthoclase, after laumontite, from Templeton, Ottawa Co., Quebec.—Some fleshed to almost white crystals, associated with pyroxene, phlogopite, and apatite, were found to have the habit and angles of laumontite, but to have the composition (anal. I) and sp. gr. of orthoclase. Pseudomorphs of this kind have previously been described from several localities in Germany, notably the so-called weissigite from Weissig, near Dresden.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	CaO.	MgO.	K ₂ O.	$\underbrace{\text{Na}_2\text{O. Li}_2\text{O.}}_{\text{Igni-}}$	tion.	Total.	Sp. gr.	
I.	63·12	19·83	0·67	—	—	0·24	15·13	0·52	0·89	100·40	2·56	
II.	43·05	30·28	3·30	0·49	1·85	6·70	3·68	0·92	—	10·70	100·97	2·6

Pseudomorph, after corundum, from Perth, Ontario.—A large crystal with the form of corundum, consists of a thin shell of tourmaline, and, in the interior, of a soft, pale green mineral with a little calcite and some scales of penninite and damourite. The pale green mineral was separated as far as possible for analysis and found to approximate in composition (anal. II) to pinite: it shows rectangular cleavages, suggesting that scapolite may have been an intermediate product in the alteration from corundum.

L. J. S.

New Occurrence of Pseudo-leucite. C. W. KNIGHT (*Amer. J. Sci.*, 1906, [iv], 21, 286—293).—Specimens of a grey rock (pseudo-leucite-phonolite) from Spotted Fawn Creek, in the Ogilvie Range, Yukon Territory, contain icositetrahedral crystals of pseudo-leucite, measuring 1 cm. across, embedded in a very fine-grained ground-mass. Both the pseudo-crystals and the ground-mass consist of a mixture of orthoclase, nephelite, scapolite, and biotite, together with a little plagioclase in the former. The orthoclase, which predominates in amount, is granular in the central parts of the pseudo-crystals, whilst in the outer portions it has the form of laths arranged roughly perpendicular to the crystal-faces. From the following analysis of the pseudo-crystals it is calculated that they contain: orthoclase, 50·04; nephelite, 32·38; anorthite, 2·22 per cent.; much of the nephelite has,

however, been altered to scapolite. The original mineral, before its alteration to orthoclase and nephelite, must have been a soda-leucite.

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O.	Cl.	Total.
58.15	23.66	1.59	0.43	0.21	7.08	8.49	1.35	trace	100.96

L. J. S.

Re-formation of Soda-leucite. T. T. READ and C. W. KNIGHT (*Amer. J. Sci.*, 1906, [iv], 21, 294—295. Compare preceding abstract).—The breaking down of metastable austenite into ferrite and cementite during the slow cooling of steel, and its reconstruction on reheating to a certain temperature, suggested that the orthoclase and nephelite of pseudo-leucite might be transformed to soda-leucite on heating a crystal to a temperature below its point of fusion. A crystal of pseudo-leucite was heated in an electric furnace at 1225° for several hours, and thin sections of the mineral afterwards examined under the microscope. The scapolite and biotite were thereby destroyed, but a considerable portion of the orthoclase and nephelite remained unaltered; a small amount of isotropic material was developed, but whether this was leucite or glass was not determined. The experiments were therefore not conclusive.

L. J. S.

Wollastonite and Pseudo-wollastonite. Polymorphic Forms of Calcium Metasilicate. EUGENE T. ALLEN and W. P. WHITE [with optical study by FRED. E. WRIGHT] (*Amer. J. Sci.*, 1906, [iv], 21, 89—108).—Wollastonite and pseudo-wollastonite are enantiotropic modifications of calcium metasilicate with an inversion temperature of 1180°. When wollastonite is heated to this temperature it becomes changed into pseudo-wollastonite, the change being accompanied by an absorption of heat, but practically no alteration in volume. For this reason attempts to prepare wollastonite artificially usually result in the formation of pseudo-wollastonite. When, however, a glass of the composition CaSiO₃ is heated at 800—1000°, wollastonite crystallises in the glass. This artificial wollastonite has a radially fibrous structure and sp. gr. 2.915, the sp. gr. of the glass being 2.905. The pseudo-wollastonite which has been formed by heating wollastonite, or which has crystallised from the molten glass, is not changed to wollastonite even when very slowly cooled or when heated under pressure with water. If, however, the pseudo-wollastonite be heated at 800—900° with fused calcium vanadate, it becomes changed to the more stable modification, and beautiful, transparent crystals of wollastonite are formed; the same result also takes place in the presence of a slight excess of lime or of silica. Pseudo-wollastonite has a sp. gr. about 2.914 and melting point 1512°; it has the form of small, irregular grains or short fibres. It is pseudo-hexagonal with a basal cleavage, and is optically positive and very nearly uniaxial; polysynthetic twinning on the basal plane and an angle of optical extinction of 2° to this plane indicate that it is probably monoclinic. The mean refractive index is very nearly the same as that of wollastonite (which, though also monoclinic, is optically negative), but the birefringence is much higher (0.025—0.035; for wollastonite, 0.015). Since neither pseudo-

wollastonite nor paramorphs of wollastonite after pseudo-wollastonite have been observed in nature, the conclusion may be drawn that the wollastonite of contact-metamorphic limestones has been formed at temperatures below 1180°. L. J. S.

Datolite from Westfield, Massachusetts. EDWARD H. KRAUS and C. W. COOK (*Amer. J. Sci.*, 1906, [iv], 22, 21—28).—A detailed crystallographic description is given of material from crevices in a trap rock at Westfield, Massachusetts. The following analysis of a clear, transparent crystal agrees closely with the usually accepted formula, HCaBSiO_5 .

SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	B_2O_3	H_2O	Total.	Sp. gr.
37.59	0.10	0.15	34.69	0.315	21.85	5.715	100.41	3.006

L. J. S.

Some Interesting Beryl Crystals and their Associations. WILLIAM E. FORD (*Amer. J. Sci.*, 1906, [iv], 22, 217—223).—The beryl crystals found in pegmatite-veins are usually green in colour and semi-transparent, and have the form of long prisms terminated by the basal plane. In certain localities, however, where the mineral occurs in pegmatite-veins in association with variously coloured tourmalines of gem quality, the crystals are pale pink or colourless and quite transparent, and in habit they are tabular or short prismatic with pyramidal planes prominently developed. Crystallographic descriptions are given of material of this kind from San Diego Co. in California, Mount Mica in Maine, Haddam Neck in Connecticut, and the Island of Elba. In these cases both the tourmaline and the beryl are rich in alkali metals, in the former lithium, and in the latter caesium predominating. Beryl from San Diego Co. was found to contain about 3 per cent., and that from Haddam Neck about 5 per cent. of alkalis. L. J. S.

Clinzoisite from Tyrol. A. H. WESTERGÅRD (*Zeit. Kryst. Min.*, 1906, 42, 279—280).—Crystals of clinzoisite from the Goslerwand, near Prägraten, were measured and the topic axes (χ , ψ , ω) calculated and compared with those of epidote from the Untersulzbachthal. It is assumed that clinzoisite is free from iron, and that in epidote $\text{Al}:\text{Fe} = 7:3$.

	Sp. gr.	Mol. vol.	χ	ψ	ω
Clinzoisite	3.344	272.5	7.482	4.720	8.551
Epidote	3.451	279.1	7.534	4.766	8.606

The replacement of aluminium by iron in the epidote molecule therefore causes an increase in all directions of the dimensions of the crystalline structure. L. J. S.

Rocks and Minerals from British Central Africa (*Bull. Imp. Inst.*, 1906, 4, 103—113).—Miscellaneous specimens belonging to two collections are individually described; they include schists and gneisses, carbonaceous shale, argillaceous concretion, and fragments of various minerals derived from these rocks. Analysis of ilmenite gave TiO_2 , 49.15; FeO , 40.93; MnO , 6.39 per cent. Analyses are also given of

coals and iron ores, and of an ore consisting largely of nickeliferous pyrrhotite (Ni, 2.75 per cent.).

L. J. S.

The Estacado Aërolite. KENNETH S. HOWARD; analysis by JOHN M. DAVISON (*Amer. J. Sci.*, 1906, [iv], 22, 55—60).—This meteoric stone, weighing 290 kilograms, was found before 1902 near Estacado, in Hale Co., Texas; a bright meteor was observed in the locality in 1882. It consists of grains and chondrules of enstatite (42.50 per cent.) and olivine (41.09 per cent.) with particles of nickel-iron (16.41 per cent.). Sp. gr. 3.63. A bulk analysis gave:

Fe.	Ni.	Co.	Cu.	S.	P.	SiO ₂ .	FeO.
14.68	1.60	0.08	trace	1.37	0.15	35.82	15.53
Total,							
	MgO.	CaO.	Al ₂ O ₃ .	Na ₂ O.	K ₂ O.	less O for S.	
	22.74	2.99	3.60	2.07	0.32	100.27	

Carbon, TiO₂, Cr₂O₃, and MnO are also present. Analyses are also given of the portions of stony matter soluble and insoluble in hydrochloric acid.

L. J. S.

Chemical Reactions in the Eruption of Vesuvius in April, 1906. JULIUS STOKLASA (*Chem. Zeit.*, 1906, 30, 740—742).—Several analyses are given of the products of the eruption, namely, of the lava, lapilli, and ash; as well as of the material extracted by water from these, and of the saline incrustations. When the lava is ignited, ammonia and other gases are evolved. In the vapours of a fumarole near the crater, the following gases were detected: hydrogen chloride, ammonia, hydrogen sulphide, and carbon dioxide, but not sulphur dioxide, although this was found to the extent of 0.01 per cent. in the volcanic ash.

L. J. S.

Fumarole Products of Vesuvian Lava. FERDINAND HENRICH (*Zeit. angew. Chem.*, 1906, 19, 1326—1328).—From a study of the vapours evolved and the incrustations deposited by the fumaroles of the recent lava streams of Vesuvius, the conclusion is drawn that the incrustations (alkali and iron chlorides) are not direct sublimation products from the lava, but rather the result of the action of water and hydrogen chloride vapours on the rock itself. In support of this it was found that samples of the newly-erupted Vesuvian lava, after being washed in water and ignited in a current of dry air, gave a sublimate of ferric chloride when ignited in a current of moist air and hydrogen chloride. Under these conditions chlorine was liberated, and this gas was also detected in the vapours of the fumaroles.

L. J. S.

Presence of Neon in the Gases of Thermal Springs. CHARLES MOUREU and ROBERT BIQUARD (*Compt. rend.*, 1906, 143, 180—182. Compare this vol., ii, 442).—The gases from twenty-two thermal springs have been spectroscopically examined for the presence of neon. In every case a positive result was obtained. In none of the gases could the neon be detected directly, however, since its spectrum is

completely masked by the argon present. The gases were therefore subjected to the action of cocoa-nut charcoal cooled to -185° or -100° before being spectroscopically examined. With the charcoal at -100° the intensity of the neon rays was considerably greater than when absorption was effected at -185° . H. M. D.

Physiological Chemistry.

Effect of Blood-pressure on Respiration. CHARLES C. GUTHRIE and F. H. PIKE (*Amer. J. Physiol.*, 1906, 16, 475—482).—The usual effect of a rise of arterial blood-pressure is an increase of respiratory rate with diminished amplitude, and of a fall, a slower rate with greater amplitude. The effect may be on the respiratory centre direct, or the increased pressure may lead to increased metabolism and a greater production of carbon dioxide which acts on the centre. Many statements on the effect of drugs, animal extracts, &c., on respiration require revision, for the agents in question may after all have no direct action on respiration, but only an indirect one through the blood-pressure. W. D. H.

Effect of Chloral Hydrate on Heart Muscle. W. H. SCHULTZ (*Amer. J. Physiol.*, 1906, 16, 483—501).—The irritability of the ventricle of frog or terrapin at first increases under the influence of chloral hydrate, then decreases, and finally disappears. During the progressive stages the refractory period shortens, but it is never entirely absent so long as the muscle remains irritable. On repeated stimulation, the curve written resembles that of incomplete tetanus. Similar curves are obtained when the heart is cooled to near 0°, when treated with ether or excess of calcium salts. The "all or nothing" law remains intact throughout. W. D. H.

Basicity of Human Blood in Health and Disease. CASIMIR VON RZENTKOWSKI (*Chem. Centr.*, 1906, i, 1834—1835; from *Arch. exp. Path. Pharm.*, 55, 47—72).—The author's investigations show that the blood owes its basicity, not merely to its mineral alkalis, but mainly to its albuminous constituents, especially those of the red corpuscles. In normal blood, the albumin-basicity of the red blood corpuscles exceeds the mineral alkalinity, but in the plasma the mineral alkalinity is the greater. T. H. P.

Filtration through Animal Membranes. The Saline Contents of the Blood compared with those of other Serous Fluids. ARTHUR F. HERTZ (*Zeit. physiol. Chem.*, 1906, 48, 347—364).—Experiments have shown that the concentration of salt in saline solutions of albumins does not decrease when filtered through

animal membranes, but the amount of albumin in the filtrate is much less than that in the original liquid. With increased pressure the percentage of albumin in the filtrate tends to diminish.

In opposition to Filehne and Biberfeld (*Pflüger's Archiv*, 1906, 91, 1) it is asserted that liquids filter through the membrane of hens' eggs. J. J. S.

The Active Constituent of Anthrax Serum. ALBERTO ASCOLI (*Zeit. physiol. Chem.*, 1906, 48, 315—330).—The immunising substance of anthrax serum passes through a Berkefeld filter. It does not behave as an amboceptor. In the serum of asses and goats it is found mainly in the pseudoglobulin fraction, and in that of goats, to a slight extent, in the euglobulin fraction. The active pseudoglobulin of asses' serum loses its protective value when kept for some time in aqueous solution. J. J. S.

Estimation of the Hæmolytic Action of Monohydric Alcohols. HERMANN FÜHNER and E. NEUBAUER (*Chem. Centr.*, 1906, ii, 137—138; from *Centr.-Bl. Physiol.*, 20, 117—119).—With the blood corpuscles of cattle at a mean temperature of 19°, it is found that each monohydric alcohol has a hæmolytic action three times as great as that of the one immediately preceding it, so that in the homologous series the activities are represented by the series, 1 : 3 : 3² : 3³, &c. The same regularity is observed in the action of the alcohols on sea-urchins' eggs and on miller's-thumbs.

Alcohols with branched chains are less active than the corresponding normal compounds. T. H. P.

Measurement of Osmotic Pressure in Small Quantities of Fluid. HARTOG J. HAMBURGER (*Biochem. Zeit.*, 1906, 1, 259—281).—Six small tubes are taken; into one is introduced 0.25 c.c. of the fluid under investigation, and into the five others the same volume of sodium chloride solutions of increasing concentration. To each is added a small volume of filtered defibrinated blood; the mixtures are shaken and left for thirty to forty-five minutes and then centrifuged. The osmotic pressure of the fluid under investigation corresponds with that of the solution of salt in which the blood corpuscles occupy the same volume as that in the fluid investigated. The method is stated to give excellent results. W. D. H.

Comparison of Conductivity and Freezing Points of Small Quantities of Body-fluids in Health and Disease. THOS. M. WILSON (*Amer. J. Physiol.*, 1906, 16, 438—467).—An electrical method, described fully, for freezing small quantities of fluid is adapted for a physical laboratory, but difficult to use clinically. The freezing point of 0.3 c.c. of salt solution can be determined fairly accurately when mercury is added to make the volume sufficient to cover the greater part of the Beckmann bulb. When the volume reaches 0.8 c.c., the mercury can be discarded. Blood and serum make, however, an emulsion with mercury, and this spoils the result.

Tables are given of the organic and inorganic constituents of the

serum, and the composition harmonises with the following six facts: (1) it represents closely the total weight of the formed substances present; (2) it represents the total alkalinity; (3) it accounts almost exactly for the five chief elements found in the salts; (4) it gives the right percentage of sodium chloride; (5) when the percentages of the salts are reduced 2 per cent. it gives the correct freezing point (0.566°); and (6) it gives the proper conductivity of normal serum (82).

An improved micagocrite is described, which gives trustworthy results; the tube can be used as an ordinary hæmatocrite.

Conductivity measurements are best made at 18° . The freezing point for gases in solution can be obtained by the equation $\Delta = 8x(10)^{-3}$, where Δ equals thousandths of a degree centigrade, and x the number of c.c. of gas dissolved in a litre of solution. The freezing-point equivalent for conductivity of serum increased 7 per cent. (given in terms of sodium chloride) gives approximately the inorganic freezing point of healthy serum (0.490°).

Various data are given in reference to serum in different diseases, but their ultimate value for diagnosis is left to future investigators.

W. D. H.

Deviation of Complement by a Serum and its Anti-serum, and its Relation to the Precipitin Test. ROBERT MUIR and W. B. M. MARTIN (*J. Hygiene*, 1906, 6, 265—285).—A mixture of serum and its anti-serum has the property of fixing or “deviating” complement, and thus interfering with hæmolysis. This is analogous to the fixation of complements by cell-receptors in association with immune bodies. A large number of different complements may be fixed by the same combination of serum and anti-serum, but some are not fixed. The amount of homologous serum necessary to produce distinct deviation is very small, 0.00001 c.c. or less, much less than is necessary to produce precipitation; but if a precipitate forms, the deviating substance is present in the precipitate. The precipitin and deviation tests give results which are in great accord as regards specificity. The deviation phenomenon produces an effect similar to an anti-complement action, and the views held on anti-complements require revision. It is an open question whether true anti-complements exist.

W. D. H.

Precipitin Anti-sera and their Standardisation. D. A. WELSH and H. G. CHAPMAN (*J. Hygiene*, 1906, 6, 251—264).—A method of standardising anti-sera is suggested. It is, however, found that whilst a certain quantity of homologous proteid completely neutralises and precipitates a given weight of precipitin anti-serum, the converse does not hold true. A given weight of proteid is not precipitated by any weight of anti-serum; a considerable portion of the proteid remains in solution, however small the quantity originally taken.

W. D. H.

Gastrotoxic Serum. CHARLES BOLTON (*Trans. Path. Soc. London*, 1906, 57, 297—312).—In response to the injection of gastric cells into an animal, the blood shows the presence of a gastric cytotoxin, which

is not only gastrolytic, but also contains a hæmolytic factor, a precipitin or precipitins, and an agglutinin or agglutinins. The gastrolytic factor does not produce solution of the cells against which it has been formed, but causes a hyaline change in them. The human gastrotoxin is of the same nature as that of the lower animals.

The final conclusion drawn is that an animal can elaborate in its blood as the result of the absorption of the tissues of a similar animal, and therefore, presumably, of its own, a poison which is potentially able to cause necrosis of the mucous membrane of its own stomach. This is regarded as of importance in relation to the pathology of gastric ulcer.

W. D. H.

Nutritive Requirements of the Body. FRANCIS G. BENEDICT (*Amer. J. Physiol.*, 1906, **16**, 409—437).—A general discussion of dietaries with special reference to the proteid requirement, and a critical examination of Chittenden's experiments and conclusions. Among the many points raised, the following observations militate against the view that a material reduction of proteid is desirable: (1) from the results of the experiments on soldiers, it is seen that the low proteid diet affected the absorption of nitrogenous material from the alimentary tract; (2) that animals fed on diets low in proteid do not thrive so well as on liberal quantities, and (3) dietary studies all over the world show that in communities where productive power, enterprise, and civilisation are at their highest, man has instinctively and independently selected liberal rather than small quantities of proteid. In many races which are often quoted as subsisting on low proteid intake, for instance, the Japanese, recent statistics show that this is not really the case. Proneness to disease is common, and disease when it occurs is more serious in its effects in those who take but little albuminous nutriment. With regard to the question of energy requirement, it is pointed out that the respiration calorimeter has furnished us with a means of measuring the energy output, and the energy output is the energy requirement, since the law of conservation of energy obtains in the animal organism. It is therefore contrary to common sense to suppose, as some writers recently have done, that a man can give forth a certain amount of daily energy and receive from his daily food an amount which is appreciably smaller and yet suffer no harm. He must call on his tissues to supply the energy which is not available from his food. This view is illustrated by data from some of the subjects of Chittenden's own experiments. The mere fact that the body weight remains constant is no proof to the contrary, for valuable material such as fat may be used up, and replaced by an equal amount of water, and excess of carbohydrate food is just the sort of diet to cause retention of water in the tissues.

W. D. H.

Action of Dextrose on the Animal Body. ERNST HEILNER (*Zeit. Biol.*, 1906, **48**, 144—231).—If dextrose dissolved in water is given by the mouth to a fasting animal in an amount corresponding with the fat catabolised during the fast, the metabolism and heat production of the animal remain unaltered. The carbohydrate given takes the

place of the fat in isodynamic quantities. If water is given without the sugar an increase in proteid and fat catabolism occurs.

If the same amount of sugar is given subcutaneously, twenty-four hours later a great diminution of catabolism and heat production takes place. This is probably the result of a harmful effect on the cells, and an alteration on their osmotic surroundings.

In only half of the rabbits experimented on did any sugar pass into the urine.

No evidence was found of any "digestion-work" in the Zuntz-Mering sense. These observers have not taken into account Rubner's views on the specific dynamic action of food-stuffs. W. D. H.

Intestinal Gases of Man. J. AUGUST FRIES (*Amer. J. Physiol.*, 1906, 16, 468—474).—More is known of the gases in the intestines of cattle and other animals than in man. In cattle, for instance, the daily production of methane is enormous, its volume (other gases not included) ranging from 100 to 250 litres and more as the feed is increased. In metabolism experiments it is therefore a factor to be reckoned with. In man, the kind of food taken, and its comparatively short stay in the body render the conditions for gas formation less favourable. Still combustible gases do escape, and the author has made some determinations of the composition of the gases; the diet was plain and moderate, and the work done not excessive. Various samples of mixed rectal gases were collected, and their composition worked out on the average: carbon dioxide, 10·3; oxygen, 0·7; methane, 29·6; and nitrogen, 59·4 per cent. by volume. The nitrogen was probably swallowed with the food. The gases were collected over water and were odourless. The total production is nearly 1 litre per diem. W. D. H.

Proteid Synthesis in the Animal Body. HUGO LÜTHJE (*Pflüger's Archiv*, 1906, 113, 547—604).—A rabbit received with its food 50 per cent. or more of its nitrogen in non-proteid form without maintaining its nitrogenous equilibrium; another received the same quantity of nitrogen in the form of potato proteid, and remained alive in nitrogenous equilibrium. The first animal was in the condition of proteid-hunger. A purely potato diet does not keep animals alive; this is due to the poverty of potatoes and similar vegetables in proteid; they can be kept alive by the addition of potato proteid to the food.

The nitrogen retention observed by Loewi and the author in dogs when they receive proteid cleavage products which no longer give the biuret reaction occurs only when simultaneously large quantities of carbohydrate (but not fat) are given also. Moreover, the same occurs when only a few amino-substances (for instance, asparagine and glycine alone) are given, which represent quite a small fraction of the proteid cleavage products. In plants also, asparagine is utilised only if sufficient carbohydrate is present too. W. D. H.

The Action of Non-proteid Nitrogenous Substances on Nitrogenous Metabolism in Animals. OSCAR KELLNER (*Pflüger's Archiv*, 1906, 113, 480—486).—A criticism on the recent work of

Lehmann (*ibid.*, 339) and of Völtz (*ibid.*, 413) on the value of asparagine in nitrogenous metabolism. The conclusion drawn by the present author, mainly from a study of Lehmann's results, is that the embedding of the asparagine in celloidin capsules to render solution slower makes no difference, and that in all cases asparagine raised proteid decomposition.

W. D. H.

Diminution of the Digestibility of Proteids. P. SALECKER and ALBERT STUTZER (*J. Landw.*, 1906, 54, 273—282).—The diminished solubility of nitrogenous substances which have been heated at temperatures below 100° seems to be due to molecular migrations in the proteid molecule rather than to the action of oxygen. The presence of peat retards digestion and is an unsuitable substance for mixing with molasses. Formaldehyde when employed as a preservative renders the proteids insoluble, but not indigestible.

N. H. J. M.

Comparative Experiments on the Natural and Artificial Digestion of Proteids. W. ROTHE, H. WANGNICK, and ALBERT STUTZER (*J. Landw.*, 1906, 54, 257—264).—Experiments with rabbits showed that the same results are obtained by natural digestion as by digestion with acid gastric juice.

N. H. J. M.

Action of Bacteria on Pepsin. J. PAPASOTIRIOU (*Arch. Hygiene*, 1906, 57, 269—272).—Pepsin in 1 per cent. solution was exposed to the action of bacteria for varying periods of time and then allowed to act on coagulated white of egg in presence of $N/10$ hydrochloric acid. In every case even nine hours' exposure was sufficient to destroy completely the activity of the pepsin. Both an infusion of putrid meat and pure cultures of *Bacillus fluorescens*, *B. putidum*, and *B. vulgare* were used.

E. F. A.

Action of Synthetical Bile Acids on the Pancreatic Decomposition of Fats. RUDOLF MAGNUS (*Zeit. physiol. Chem.*, 1906, 48, 376—379).—Bondi and Müller's synthetical glycocholic and taurocholic acids (this vol., i, 633) in the form of their sodium salts considerably increase the activity of pancreas lipase, although they are without effect on lipase from the intestine or stomach.

J. J. S.

Decomposition of Leucine Esters by the Pancreatic Ferment. OTTO WARBURG (*Zeit. physiol. Chem.*, 1906, 48, 205—213. Compare Abstr., 1905, i, 176).—Leucine ethyl ester is asymmetrically hydrolysed by pancreatin even when the lipase is removed. This removal is accomplished by subjecting the pancreatin to auto-digestion at the ordinary temperature and in the presence of toluene for twenty-three hours, or more completely still when 0.02*N* sodium hydroxide is used instead of water.

The hydrolysis is a convenient method for the preparation of *L*-leucine.

Leucine n-propyl ester boils at 95—96° under 12 mm. pressure.

J. J. S.

Influence of Neutral Salts on the Peptic Hydrolysis of Albumin. S. LEVITES (*Zeit. physiol. Chem.*, 1906, 48, 187—191).—The effect of the following salts on the peptic digestion of blood-fibrin and of crystallised egg-albumin has been studied. Lithium, sodium, potassium, calcium, and strontium chlorides; sodium and potassium bromides; potassium iodide; lithium and sodium sulphates, potassium oxalate, and the sodium salts of malonic, acetic, propionic, and butyric acids. Practically all the salts retard the hydrolysis, and this retardation increases with the concentration of the saline solution. The action of the salt appears to be due to the acid and not to the metallic radicle present, and in the case of salts with the same metallic but different acid radicles the effect is inversely proportional to the affinity constants of the acids from which the salts are derived.

J. J. S.

Secretion of Lithium in the Urine and Decomposition of Lithium Iodide in the Organism. FR. BERGER (*Chem. Centr.*, 1906, i, 1837; from *Arch. exp. Path. Pharm.*, 55, 1—15).—When 1 gram of lithium chloride, dissolved in 50 c.c. of water, is administered, three-fourths of it are eliminated in the urine in fifty-four hours, and even after three days 7 per cent. of it still remains in the body. The last residue is only very slowly secreted and the salt may be detected in the urine up to the seventh day after administration. Similar behaviour is met with when lithium iodide is employed, the secretion being somewhat more rapid than in the case of the chloride. Both the salts leave the body almost quantitatively by the kidneys.

When lithium iodide is administered, the secretion of the iodine is quite independent of that of the lithium; it reaches its highest value in the second hour, and afterwards falls regularly. The lithium curve, however, reaches its highest point in the third hour, then falls, and in the seventh hour exhibits a peak of the same height as the first. The iodine is secreted more rapidly than the lithium, but a greater proportion of the latter is ultimately eliminated. The secretion of the iodine is the same, whether it is taken as sodium or lithium salt.

T. H. P.

Behaviour of Quinoline in the Animal Body. I. HERMANN FÜHNER (*Chem. Centr.*, 1906, i, 1835—1837; from *Arch. exp. Path. Pharm.*, 55, 27—38. Compare Abstr., 1905, i, 828).—The author has previously found that, after ingestion of quinoline, the urine, when boiled with hydrochloric acid and tested with ammonia, gives a green coloration. This reaction is much more marked if the quinoline derivative to which it is due is first isolated in the pure form; the method of doing this is described.

Further investigations indicate the identity of this quinoline derivative with 5:6-quinolinequinone (compare Matheus, Abstr., 1888, 965), which forms groups of almost colourless prisms, melting at above 350° and dissolving slightly in water or organic solvents. It dissolves readily in acetic acid or mineral acids, giving a typical quinone coloration. Its salts are not dissociated by water. The addition of a trace of alkali hydroxide to absolute alcoholic solutions of the base or its salts gives a green coloration, which changes rapidly

to violet, red, and yellow in succession. Acetic acid solutions of the quinolinequinone condense in the cold with excess of aniline, giving : (1) a chlorophyll-green *anilide* separating in flocks of slender needles melting at above 350° ; (2) an azine. The quinolinequinone could not be reduced to the corresponding quinol.

Besides 5:6-quinolinequinone, at least three other products are present in the urine after administration of quinoline. T. H. P.

The Amount of Amino-acids in Normal Human Urine.

L. MOHR (*Zeit. physiol. Chem.*, 1906, **48**, 380—381).—Reply to Abderhalden and Schittenhelm (this vol., ii, 470). J. J. S.

Excretion of Amino-acids in Diabetic Urine. EMIL ABDERHALDEN and ALFRED SCHITTENHELM (*Zeit. physiol. Chem.*, 1906, **48**, 574—576).—Polemical against L. Mohr. W. D. H.

The Amount of Urea in Normal Human Urine. WM. OVID MOOR (*Zeit. physiol. Chem.*, 1906, **48**, 577—579).—Polemical against Lippich (this vol., ii, 564). W. D. H.

Action of Diphtheria and Diphtheria-like Bacilli. GEORGE S. GRAHAM-SMITH (*J. Hygiene*, 1906, **6**, 286—295).—A large number of diphtheria-like organisms was examined and contrasted with the true diphtheria bacillus. Most produce less acid than the diphtheria organism. Hofmann's bacillus and a diphtheria-like bacillus from the normal ear form no acid at all. Many act on mannitol and on sucrose, and so can be distinguished easily from the diphtheria bacillus, which has no action on these two substances. W. D. H.

A New Pathogenic Bacillus isolated from an Enlarged Prostate Gland. LEONARD S. DUDGEON (*J. Hygiene*, 1906, **6**, 296—299).—A bacillus resembling the colon bacillus was separated from an enlarged prostate gland. Cultural tests which are fully described distinguish it, however, from any known organism. W. D. H.

Antipyretic Action of *iso*Succinic Acid Derivatives of Aniline, *p*-Toluidine, and *p*-Aminophenol. CARMELO MALERBA (*Chem. Centr.*, 1906, ii, 349—350; from *Arch. Farmacol. sper.*, **5**, 267—280).—Although no antipyretic action is exerted by the *iso*-succinic acid derivatives of aniline and *p*-anisidine, the derivatives of *p*-toluidine, especially *p*-tolylisossuccinic acid, have a slight, and those of *p*-phenetidine, especially di-*p*-ethoxyphenylisossuccinodiamide, a stronger, antipyretic action. A hæmolytic action runs parallel with the latter. T. H. P.

Therapeutic Application of Quinine Formate. P. PICCININI (*Chem. Centr.*, 1906, ii, 351; from *Boll. Chim. Farm.*, **45**, 330—332).—Basic quinine formate, $C_{20}H_{24}O_2N_2 \cdot HCO_2H$, crystallises in shining, white needles melting at 132° and is levorotatory. Eighty-eight per

cent. alcohol dissolves one-third of its weight of the salt at 20°; chloroform, 12 parts per 100; water, 5 parts per 100; ether, traces; in olive oil, it is insoluble. The aqueous solution gives with ammonia a white precipitate insoluble in excess of ammonia, and with alkali hydroxide or carbonate a white, insoluble precipitate. The addition of bromine water and a few drops of potassium ferrocyanide solution to the aqueous solution of the salt causes the formation of a pale green precipitate, which, in presence of ammonia, turns red and subsequently greenish-violet.

Administration of 0.1—0.2 gram of the salt, dissolved in water or dilute alcohol (10—20 per cent.), in the form of a subcutaneous injection is not to be recommended.

T. H. P.

Injection of Benzidine Dyes into Normal Animals. G. BOUFFARD (*Ann. Inst. Pasteur*, 1906, 20, 539—546).—A dose of 1 centigram of the azo-dye from tolidine + H acid injected subcutaneously has no deleterious effect on mice. The colour is rapidly absorbed and remains fixed for some time; it circulates for some twelve days, and is eliminated through the intestine and different glands, especially through the kidneys, and may be detected in the urine when it is impossible to do so in the serum. Descriptions of the various tissues as coloured by the dye are given.

A guinea-pig can withstand 20 centigrams of the dye and a rabbit 30. The general action of the dye is similar to that of other benzidine dyes.

J. J. S.

The Inhibition of the Toxic Action of Hypertonic Solutions on the Sea Urchin's Egg by Potassium Cyanide and Diminution of Oxygen. JACQUES LOEB (*Pflüger's Archiv*, 1906, 113, 487—511).—Hypertonic solutions of certain concentration produce cytolysis by the withdrawal of water from the cells. This is not inhibited either by diminution of oxygen or by potassium cyanide, but accelerated. But if the hypertonic solution is less concentrated, a toxic action is exerted, and manifests itself by abnormal development, or if the exposure has been longer by the rapid death of the egg, when it is placed again in normal sea water. This form of poisoning only occurs if the hypertonic solution contains free oxygen, and is largely inhibited by withdrawal of oxygen or the addition of potassium cyanide, and to a less degree by small quantities of acids; it is accelerated by small amounts of alkali. The action is attributed to the effect of the reagents on oxydases which are considered to play a part in the oxidation processes of cell life.

W. D. H.

The Absorption of Methylene-blue by the Intestinal Epithelium. GUSTAV SCHMIDT (*Pflüger's Archiv*, 1906, 113, 512—528).—After administration of solutions of methylene-blue by the mouth, in concentrations as low as 1 in 10,000, the cells of the intestinal epithelium contain blue-coloured granules in which the concentration of the pigment must be at least 200 times as great as in the solution given. In winter frogs these are observable from four hours to forty-two days after the feeding. The appearance of the granules probably goes hand in hand with the death

of the cells. The granules also contain fat ; outside the body, however, fat-drops do not take up methylene-blue.

W. D. H.

Action of Alkaloids on Cockroaches. LAD. MICHALSKI (*Bull. Acad. Sci. Cracow*, 1905, 635—668).—The effect of various poisons on cockroaches has been investigated. Salts of various alkaloids were introduced (*a*) with the food, (*b*) by injection into the body cavity, (*c*) by injection *per anum*. The action on different individuals varies considerably, especially with dilute solutions or feeble poisons. The effect in most cases, with the exception of quinine, is least noticeable when the alkaloid is injected *per anum*. In all cases the action is far less marked than with higher animals, and an alkaloid like muscarine, which is highly poisonous to the higher forms of animal life, has but little effect on cockroaches. The following list of alkaloids is arranged in order of increasing activity as regards cockroaches. Muscarine, morphine, atropine, *apomorphine*, quinine, pilocarpine, caffeine, cocaine, strychnine, nicotine, veratrine.

J. J. S.

Chemistry of Vegetable Physiology and Agriculture.

Culture of Micro-organisms in Definite Chemical Media. J. GALIMARD, L. LACOMBE, and ALBERT MOREL (*Compt. rend.*, 1906, 143, 349—350).—The original contains a list of the micro-organisms cultivated in a medium consisting of water (100 grams), sodium chloride (0.5 gram), magnesium sulphate (0.05 gram), calcium glycerophosphate (0.2 to 0.3 gram), glycerol (1.5 grams), sufficient potassium hydrogen carbonate to render the solution alkaline, and 1 to 2 per cent. of a pure amino-acid or a definite mixture of such acids prepared by hydrolysis of different proteid matter and purified by the method previously described (Hugounenq and Morel, this vol., i, 719). The following amino-acids were thus employed: glycine, tyrosine, aspartic acid, arginine hydrochloride, lysine hydrochloride, or a mixture of leucine (75 per cent.) and alanine (25 per cent.) with a trace of tyrosine. M. A. W.

Influence of Carbon Dioxide under High Pressure on the Bacteria in Water and in Milk. W. HOFFMANN (*Arch. Hygiene*, 1906, 57, 379—399).—River water has been exposed to high pressures of carbon dioxide, up to seventy-five atmospheres, in a specially constructed apparatus, and the number of bacteria determined before and after treatment. It is found that after twenty-four hours' exposure to pressures of fifty atmospheres at low temperatures, the bacteria are destroyed practically entirely; in fact no cultures developed on a solid nutrient even after allowing the treated water, enriched with

a peptone salt solution, to remain for twenty-four hours. Similarly, aqueous infusions of cholera and typhus bacilli are totally destroyed by three hours' exposure to carbon dioxide at fifty atmospheres.

When milk is exposed to this pressure at a temperature of 56°, the casein is coagulated and separates from the serum. The bacteria, however, are not entirely destroyed by the treatment, cultures in every case appearing on a solid nutrient.

Fresh milk treated in this manner coagulates some twenty-four to forty-eight hours later than normal milk.

Agglutins in dilute serum are not injured by exposure to the carbon dioxide, but bacteria accidentally present are destroyed.

E. F. A.

Action of Compressed Gases on the Life of Micro-organisms and on Enzymes. CARLO FOÀ (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 53—58).—The author has studied the action of oxygen, hydrogen, and carbon dioxide, compressed under 2, 3, 4, or 5 atmospheres, on *Bacillus subtilis*, *Saccharomyces invertens*, *Sarcina aurantiaca*, *B. typhi*, and *Saccharomyces cerevisiae*.

Hydrogen under four atmospheres' pressure, and in presence of oxygen at the normal partial pressure, has no harmful action, either on the life of the micro-organisms or on the activity of enzymes or toxins. Oxygen or carbon dioxide at the same pressure prevents the development of the micro-organisms, provided that the surface on which they act is great relatively to the mass of the culture; they have, however, no action on enzymes or toxins, except in the case of carbon dioxide, which, under a pressure of four atmospheres, inhibits the fermentative action of zymase solution.

T. H. P.

Anaërobic Respiration, Alcoholic Fermentation, and Formation of Acetone in Seedlings. WLADIMIR PALLADIN and S. KOSTYTSCHEW (*Zeit. physiol. Chem.*, 1906, 48, 214—239).—It is shown that a considerable amount of alcohol is formed during the anaërobic respiration of living lupin seeds and seedlings, and the process is thus identical with alcoholic fermentation. With frozen lupin seeds or seedlings and the stalks of *Vicia Faba* no appreciable amount of alcohol is formed during anaërobic respiration.

With living and frozen peas, ricinus seeds, and maize, a certain amount of alcohol is formed. With living peas the alcohol only collects in the absence of oxygen, but with frozen peas considerable quantities of alcohol are formed, either in the presence or absence of oxygen. This is attributed to the fact that by the process of freezing, although the plant is killed, the zymase is not destroyed, but the oxidising processes in the cells are much retarded.

Acetone and other products which colour Schiff's reagent are also frequently formed during anaërobic respiration.

J. J. S.

An Exclusively Anaërobic Sarcina. MARTINUS W. BEYERINCK (*Arch. Néerland.*, 1906, [ii], 11, 199—205).—The sarcina is grown in a broth containing 3—10 per cent. of glucose acidified by the addition of 6—10 c.c. of normal phosphoric acid, and infected with a considerable

quantity of earth, so as to form a layer of nearly 1 cm. thickness at the bottom of the flask. This is set aside at 37° in closed vessels, when an energetic fermentation takes place, and a scum forms on the liquid. The liquid is almost free from organisms, but the sediment is a mass of sarcina, the cells measuring 3.5 μ , and being among the largest sarcinae known. The scum consists of a mucus, the cell walls of which are composed of cellulose, and are coloured a bluish-violet by zinc chloride and iodine. The gas produced is a mixture of 75 per cent. of carbon dioxide with 25 per cent. of hydrogen. A practically pure culture is at once obtained when the mass of earth is large (and this also prevents the access of air to the culture) and the acidity is within the proper limits. Sucrose and dextrose are available as nutrients, not, however, lactose or mannitol. Peptones are the only source of useful nitrogen, carbamide or asparagine and similar simple substances being useless. The sarcina can be dried without losing its vitality.

E. F. A.

Oxidation of Hydrogen by Micro-organisms. HERMANN KASERER (*Centr. Bakt. Par.*, 1906, 16, ii, 681—696, 769—775).—*Bacillus pantotrophus*, which occurs in soils, oxidises hydrogen indirectly by accelerating the reduction of carbon dioxide to formaldehyde by it; this is due to the bacillus utilising the formaldehyde as food.

Bacillus oligocarbophilus is able to respire carbon monoxide and, in symbiosis with other microbes, to oxidise hydrogen. The oxidation of hydrogen is explained by the catalytic reduction of carbon dioxide to monoxide by hydrogen being expedited by the consumption of the carbon monoxide by the microbe.

Assimilation of carbon dioxide can take place (1) by reduction to formaldehyde, as in the case of *B. pantotrophus*, and probably green plants; and (2) by reduction to carbon monoxide, as in the case of *B. oligocarbophilus* and, as would seem probable, the other known autotrophic microbes.

N. H. J. M.

Decomposition of Oblitine by means of Bacteria. I. FRIEDRICH KUTSCHER (*Zeit. physiol. Chem.*, 1906, 48, 331—333).—When a faintly acid solution of oblitine chloride is kept for twenty-four hours, it undergoes bacterial decomposition, and becomes strongly alkaline. From the product, oblitine aurichloride melting at 107°, novaine aurichloride melting at 153°, and a third aurichloride decomposing at 285° have been isolated.

J. J. S.

Relations of Oxygen and of Movement of the Nutrient Solution to the Increase and Fermentative Activity of Yeast. LEOPOLD NATHAN and WILLY FUCHS (*Chem. Centr.*, 1906, ii, 63; from *Zeits. ges. Brauw.*, 29, 226—234, 243—252, 282—289, 299—304, and 312—321).—The authors' experiments, made with the Hansen apparatus, lead to the following results: an abundant supply of oxygen does not exert any appreciable favourable influence on the fermentative activity of yeast, but causes an increase in the activity of budding. A small quantity of oxygen introduced into an oxygen-free nutrient solution excites renewed fermentative activity in the yeast, without budding taking place. Regular motion of the nutrient

liquid accelerates fermentation by producing larger surfaces of contact between the wort and yeast, and causes the growth of an increased quantity of well-nourished, vigorous yeast. The amount of oxygen absorbed from a nutrient solution is several times that necessary to the fermentation. By diminishing the aëration or the oxygen content of the liquid, the increase in the amount of yeast produced by agitation of the solution can be annulled; the fermentation is then effected in a shorter time and without any considerable amount of extract being given up to the yeast. The carbon dioxide produced during fermentation is capable of diminishing, to a slight extent, the budding power of the yeast, but it has no influence on the fermentative activity of the cells, provided the latter are sufficiently well supplied with food. If the shaking is continued beyond a certain limited time, the fermentative and budding powers of the cells cease and the yeast dies.

T. H. P.

Anaërobic Nitrogen-absorbing Bacteria. EMIL HASELHOFF and G. BREDEMANN (*Chem. Centr.*, 1906, i, 1896—1897; from *Landw. Jahrb.*, 35, 381—414).—The authors have studied the occurrence and distribution of anaërobic bacteria, their capability of fixing the nitrogen of the air, and their morphological characters. The presence of nitrogen-fixing *Clostridium* forms was detected in nearly all the samples of soil and leaf-mould examined. Nitrogen assimilation experiments made with both crude and pure cultures indicate, in some cases, the absorption of quite considerable amounts of nitrogen, similar to those observed by Winogradsky in his experiments on *Clostridium Pasteurianum*. Morphologically, the forms isolated by the author (*Clostridium* α to ϵ) are extraordinarily similar, but exhibit marked differences both from one another and from *Clostridium Pasteurianum*.

The authors guard themselves against assuming that their results are to be regarded as a recommendation to the inoculation of soil with nitrogen-fixing bacteria.

T. H. P.

Velocity of Fermentations. III. REGINALD O. HERZOG (*Zeit. physiol. Chem.*, 1906, 48, 365—375. Compare Abstr., 1904, ii, 164, 506; 1905, i, 164).—Mainly a review and criticism of recent views on the velocity of fermentations.

J. J. S.

Bactericidal and Antiseptic Influence of Stable 3 per cent. Hydrogen Peroxide. BODO SCHMIDT (*Chem. Centr.*, 1906, ii, 145; from *Hygien. Rundsch.*, 16, 517—528).—By rinsing the mouth with 3 or 1 per cent. hydrogen peroxide (Merck's perhydrol) solution, the number of germs is considerably diminished.

Various kinds of bacteria in high concentrations in physiological sodium chloride solution, when placed in contact with a 1 per cent. hydrogen peroxide solution, undergo marked diminution in numbers after one to three minutes, and are completely destroyed in five to ten minutes. With wine yeast and red yeast, a few cells remain undestroyed after twenty-five minutes, and the same is the case with a virulent culture of *Staphylococcus pyogenes aureus* after an hour. A 2 per cent. hydrogen peroxide solution kills the bacteria after three to

ten minutes, and red yeast and the *Staphylococcus* after fifteen minutes, whilst with wine yeast twenty minutes is insufficient. The 3 per cent. solution destroys most bacteria after 0·5—5 minutes, whilst some types of wine yeast persist even after ten minutes. *Staphylococcus* is killed by the 3 per cent. solution even in meat-extract cultures. Pure cultures of *B. acidi lactici* introduced into the mouth are mostly killed by rinsing with a 1—3 per cent. peroxide solution for three to five minutes.

In much lower concentrations than the above named, hydrogen peroxide prevents multiplication and fermentation. T. H. P.

Influence of Mycoderma on the Reproduction and Fermentation of the Yeasts. I. ALEXANDER KOSSOWICZ (*Chem. Centr.*, 1906, ii, 144; from *Zeit. landw. Vers. Wes. Österr.*, 9, 688—692).—The growth and fermentative activity of yeast in solutions containing sucrose and salts are greatly favoured by the presence of moulds or mycoderma, although the latter may not be able of themselves to bring about fermentation. These organisms are able to assimilate the nitrogen of ammonium salts, and excrete large quantities of invertase. A very small amount of yeast, which showed a very slight reproduction and no visible fermentation, multiplied a thousand times more strongly and produced vigorous fermentation when mixed with a few mycoderma cells.

Pressed yeast and wine yeasts are almost always brewery yeasts, and are frequently contaminated with mycoderma. T. H. P.

Fermentative Production of Coumarin during Development of Certain Hyphomycetes. B. GOSIO (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 59—62).—Many of the hyphomycetes are capable of converting aliphatic compounds into substances of the aromatic series. When *Aspergillus glaucus*, *A. varians*, or *A. fumigatus* is cultivated in Raulin's solution, the acidity of the latter is neutralised, and a large excess of alkali produced. Further, the solution gives colour reactions indicating the presence of coumarin, which is formed at the expense of the carbohydrate. T. H. P.

Bacteria of "Blown" Tins of Preserved Food. EDWARD P. CATHCART (*J. Hygiene*, 1906, 6, 248—250).—In the samples of "blown" tins examined, organisms of an intestinal type were present, which on re-inoculation into sound tins led to gas formation. No toxic symptoms were produced by feeding guinea-pigs on the contents (sardines, salmon, beef) of the tins. W. D. H.

Bacteriology of Milk. ALFRED MACCONKEY (*J. Hygiene*, 1906, 6, 385—407).—With ordinary care, fresh milk can be obtained containing less than 1500 organisms per c.c. It should not contain gas-forming organisms in 50 c.c. These are the result of faecal contamination. Particulars are given as to the varieties of organisms met with. New tests suggested are fermentation with dulcitol, adonitol, inulin, and Voges and Proskauer's reaction as substitutes for some of the older methods of routine work. W. D. H.

Reduction of Methylene-blue by Cow's Milk. EDWARD P. CATHCART (*J. Hygiene*, 1906, 6, 300—303).—A mixture of formaldehyde and methylene-blue is decolorised by fresh milk. This is due to the presence of a catalase in milk which is readily destroyed by heat. The reaction therefore serves excellently to distinguish fresh from boiled or heated milk, but is too delicate for ordinary use in estimating bacterial contamination. W. D. H.

Oxidising and Reducing Properties of the Living Cell. II. Extracellular Oxydases. M. RACIBORSKI (*Bull. Acad. Sci. Cracow*, 1905, 668—693. Compare Abstr., 1902, ii, 419; this vol., ii, 45).—The living cells of *Alternaria tenuis* produce an oxydase which closely resembles laccase (Abstr., 1895, i, 385, 386; 1896, ii, 61, 268; 1897, ii, 117; 1898, i, 53, 128; 1899, i, 313; ii, 444). The filtrate from a culture of the organism gives the characteristic reactions more readily than the cells themselves. The oxydase is precipitated by the addition of 50—75 grams of ammonium sulphate to 100 c.c. of the oxydase solution. Very dilute solutions of benzidine and of α -naphthylamine diffuse through the roots of various plants and become oxidised in the tracheæ.

Experiments made with various plants by aspirating distilled water through the leaves indicate that the surface of many cells is coated with an oxydase similar to laccase. The oxydase is very different from most enzymes: it more closely resembles peroxides or quinones, and causes the oxidation of numerous benzene derivatives, but not of dextrose, tyrosine, phenylalanine, or potassium iodide. Its activity is largely destroyed by hydroxylamine, hydrocyanic acid, or potassium sulphite, but is accelerated by the addition of small amounts of zinc, nickel, cobalt, and manganese salts, and of ferro- and ferri-cyanides.

J. J. S.

Oxidising and Reducing Properties of the Living Cell. III. The Iodide Reaction of *Aspergillus niger*. M. RACIBORSKI (*Bull. Acad. Sci. Cracow*, 1905, 693—707).—In the case of *Aspergillus niger*, the formation of an extracellular oxydase is dependent on the stage of development of the mould and also on the carbon contents of the nutrient solution. The liberation of iodine is not due to a laccase, to nitrous acid, or to a quinone, but to a substance which is termed an *iodide-oxydase*.

J. J. S.

Estimation of Choline and Betaine in Plant Tissues, and Observations on Lecithins. VLADIMÍR STANĚK (*Zeit. physiol. Chem.*, 1906, 48, 334—346).—The method already described (this vol., ii, 314) has been adapted for estimating choline and betaine in plant tissues. Betaine is present in rye, barley, wheat, horse beans, lentils, beet, rye plants, and fresh and dry beet leaves. Oats contain no betaine, and peas contain trigonelline in place of betaine. Practically all the above contain choline with the exception of beet leaves some seven months old. The amount of choline is small in most cases and falls below that required for the amount of lecithin usually soated to be present. Most specimens examined were two years old. J. J. S.

Amount of Solanine in Potatoes. M. WINTGEN (*Zeit. Nahr. Genussm.*, 1906, 12, 113—123).—The amount of solanine varies in different varieties of potatoes and is less than is indicated by previous analyses. The highest and lowest results in 1898 and 1899 were 0.1059 and 0.0172 part per thousand. No increase in the amount was observed after prolonged storage, even in germinated potatoes when the shoots were carefully removed. Diseased potatoes do not seem to contain more solanine than healthy ones.

The production of solanine by bacteria on potato observed by Weil was not confirmed.

The amount of solanine in potatoes is so small that any poisonous effect would seem to be out of the question. N. H. J. M.

Medicinal and Useful Plants of Brazil. II. THEODOR PECKHOLT (*Chem. Centr.*, 1906, ii, 136—137; from *Ber. deut. pharm. Ges.*, 16, 176—192. Compare this vol., ii, 484).—The author gives the composition of the useful parts of *Jatropha Curcas*, *Jatropha multifida*, *Jatropha oligandra*, *Mabea fistuligera*, *Ophthalmoblaston macrophyllum*, *Ophthalmoblaston pedunculare*, and *Sapium biglandulosum* var. *Klotzschiana*. T. H. P.

Detection and Estimation of Syringin in the Various Organs of Lilac and Privet. J. VINTILESCO (*J. Pharm. Chim.*, 1906, [vi], 24, 145—154).—The glucoside syringin may be readily isolated from the leaves, bark, flowers, and stem of the lilac, also from the leaves and bark of the privet, by extracting the aqueous decoction with ethyl acetate. The glucoside may then be recognised by its melting point (190—192°), the intense reddish-violet coloration with sulphuric acid, and by its rotatory power $[\alpha]_D - 17^\circ$.

When treated repeatedly with emulsin, it is quantitatively resolved into syringenin, which is insoluble in water, and dextrose, which affords a suitable means for its estimation. L. DE K.

Food Value and Digestibility of Oat, Lentil, and Pea Husks. FR. HONCAMP (*Landw. Versuchs-Stat.*, 1906, 64, 447—476).—Woody and siliceous husks, such as those of oats and lentils, have lower food values than the corresponding straws; in the case of lentils, the amount of digestible matter is so small that it is hardly sufficient to cover the amount consumed in the process of chewing. Pea husks, on the other hand, have a food value at least equal to that of the straw, and it may be assumed that this holds good more or less in the case of many other leguminous plants. N. H. J. M.

Malt Germs. FERDINAND BARNSTEIN (*Landw. Versuchs-Stat.*, 1906, 64, 435—446).—A summary of results by different investigators relating to the composition and food value of malt germs. N. H. J. M.

Chemical and Physical Action of Brine on Soil. D. J. HISSINK (*Chem. Centr.*, 1906, ii, 352; from *Chem. Weekblad*, 3, 395—403).—From a chemical point of view, salt water in small

quantities may be useful to soil, as it brings into a soluble form salts, such as calcium sulphate, calcium and magnesium phosphates and carbonates, and certain silicates, useful to plant life. In large quantities, however, salt water dissolves the valuable constituents of soil and carries them away unused, and may hence be regarded as a plant-poison.

Physically, the change produced in soil by brine is a breaking-down similar to that effected by frost. But, here again, large quantities of water have an unfavourable influence, since they have the opposite effect. The salt, too, forms an incrustation on the soil, thus differing from lime, which is less soluble in water.

T. H. P.

Availability of Phosphoric Acid of the Soil. GEORGE S. FRAPS (*J. Amer. Chem. Soc.*, 1906, 28, 823—834).—Aluminium, iron and calcium phosphates, phosphorite, vivianite, triplite, and apatite dissolve completely in $N/5$ hydrochloric and nitric acids under soil conditions; some also dissolve completely in $N/50$ and $N/200$ hydrochloric acid and in 1 per cent. citric acid.

Other soil constituents when dissolved expose physically unavailable phosphoric acid to the action of the solvent. Calcareous soils thus differ from siliceous soils, and it is necessary to group soils according to the total soluble matter extracted by the solvent.

Soils fix phosphoric acid dissolved in water, carbonated water, and acetic acid; aluminium and ferric hydroxides, under soil conditions, fix phosphoric acid from $N/50$ nitric acid, and it is possible that when this solvent is employed some of the phosphoric acid is removed by the soil.

Experiments with cow-peas in four different soils showed that the plants removed from 17 to 60 per cent. of the phosphoric acid soluble in $N/5$ nitric acid. Comparing the assimilative power of rice, cotton, maize, and cow peas, it was found that maize had the lowest, rice the next solvent power, whilst cotton and cow peas were about equal.

Experiments with fifteen soils seemed to indicate a relation between the phosphoric dissolved by $N/5$ nitric acid and the soil deficiencies as shown by pot cultures.

N. H. J. M.

Effect of Straw Manure on the Crops. CONRAD VON SEELHORST (*J. Landw.*, 1906, 54, 283—300. Compare Abstr., 1904, ii, 439).—Straw, in absence of sodium nitrate, always caused a diminished yield, especially in the case of poorer sandy and loamy soils. The effect of straw was relatively slight on fertile soils. In presence of sodium nitrate, straw proved to be beneficial in the case of fertile soils.

Injury by straw manuring is almost always confined to the first year, and continues in the second and third years only in the case of poor, sandy soils. On loamy soils, and in conjunction with sodium nitrate on sandy soils, the yield is somewhat increased in the second and third years after application of cut straw, so that the loss in the first year is more or less recovered.

N. H. J. M.

Manurial Experiments with "Agricultural-Phosphate." HERMANN BACHMANN (*J. Landw.*, 1906, 54, 301—307. Compare Abstr., 1904, ii, 145).—Experiments on sandy soil with amorphous

“agricultural-phosphate” and apatite showed that the action of apatite ceased after the first year, whilst the amorphous phosphate was almost equal to basic slag both in the first and second year.

N. H. J. M.

Analytical Chemistry.

Preparation of Standard Solutions. SALOMON F. ACREE and R. F. BRUNEL (*Amer. Chem. J.*, 1906, **36**, 117—123).—A standard hydrochloric acid, the error of which does not exceed 0.05 per cent., is prepared by passing hydrogen chloride, generated from ammonium chloride by the action of concentrated sulphuric acid, into a weighed amount of conductivity water. Standard solutions of other anhydrous gases: hydrogen bromide, iodide, or sulphide, sulphur dioxide, ammonia, chlorine, or standard alcoholic hydrogen chloride, may be prepared similarly. *N/5* ammonium hydroxide loses ammonia quickly when exposed to the air or during transference to other vessels.

The strength of solutions of acids, the sodium salts of which can be dried and accurately weighed, is determined best by titration with pure sodium hydrogen carbonate in presence of methyl-orange until the solution remains faintly pink in a vacuum, evaporation of the resulting solution, and weighing of the residual sodium salt. The strength of potassium or sodium hydroxide solution is determined similarly by evaporation with pure hydrochloric acid. The total errors of this method do not exceed 0.05 per cent.

Methyl-orange is found to be more sensitive to carbon dioxide than is generally supposed. G. Y.

Variable Sensitiveness in Colorimetry. II. DAVID W. HORN and SUE A. BLAKE (*Amer. Chem. J.*, 1906, **36**, 195—208. Compare this vol., ii, 253).—A series of colorimetric experiments with copper sulphate solutions has been made similar to the experiments with potassium chromate. The results, which are tabulated and expressed by curves, show that the amount of copper sulphate which will produce at different concentrations a difference in colour that can just be distinguished is a constant fraction of the total weight of copper sulphate present; it follows that the sensitiveness varies inversely as the total copper. Exceptions to this rule occur when the solutions are too dilute or too concentrated. Whenever the difference in colour between two copper sulphate solutions is just perceptible, the ratio between the two quantities of copper is always the same.

Every colorimetric method possesses at least one maximum of sensitiveness, and solutions may be too concentrated or too dilute to give accurate analytical results, which can be obtained only within certain limits of concentration; between these limits the percentage error is constant. G. Y.

Modification of the Methyl-violet Process in the Estimation of Free Mineral Acids. ANDREA CORSINI (*Chem. Centr.*, 1906, ii, 69; from *Giorn. Farm. Chim.*, 55, 200—205).—For estimating free mineral acids the author proposes the use of Tropeolin OO, in alcoholic solution, in place of methyl-violet. The change of colour from yellow to reddish-violet is more distinct and more sensitive than with the latter indicator. The change is produced by acids of the following concentrations: sulphuric acid, 1 : 20,000; nitric acid, 1·1 : 10,000; hydrochloric acid, 2·5 : 10,000. In acetic acid, the change of colour is caused by concentrations rather less than 0·5 : 1000 for sulphuric acid, 1·5—2 : 1000 for nitric acid, and 2—2·5 : 1000 for hydrochloric acid.
T. H. P.

Estimation of Hydrogen Peroxide, Ferrous Salts, and other Reducing Agents. W. E. MATHEWSON and J. W. CALVIN (*Amer. Chem. J.*, 1906, 36, 113—117).—The strength of hydrogen peroxide solutions may be determined by dilution to about 0·2*N* and titration against ferrous ammonium sulphate in presence of ammonium sulphate and a small amount of phosphoric acid; a solution prepared by fusing titanium dioxide with potassium hydrogen sulphate and dissolving the product in cold dilute sulphuric acid is used as the indicator.

The titration of sodium nitrite in 0·5—0·2*N* solution with hydrogen peroxide in presence of titanium sulphate gives concordant but slightly high results.
G. Y.

Estimation of Ammonia in Waters by means of Nessler's Reagent. ALBERT BUISSON (*Compt. rend.*, 1906, 143, 289—291).—When Nessler's reagent is added to a dilute solution of ammonium chloride (0·006 gram of NH_3 per litre) a brown precipitate is slowly deposited, and the colourless filtrate contains 21 per cent. of the original ammonia. The precipitate consists of 14 per cent. of mercuric iodide together with the compound $\text{Hg}_9\text{N}_4\text{I}_6$ (compare François, *Abstr.*, 1900, ii, 142, 208, 280), which is insoluble in ordinary neutral solvents, soluble in potassium iodide, but decomposed by excess of the reagent according to the equation $\text{Hg}_9\text{N}_4\text{I}_6 + 12\text{KI} + 12\text{H}_2\text{O} = 9\text{HgI}_2 + 12\text{KOH} + 4\text{NH}_3$; the inverse of the equation represents the formation of the precipitate under the original conditions. The reaction therefore between Nessler's reagent and a dilute solution of an ammonium salt is a reversible one, and the method of determining the amount of ammonia in a water by estimating the mercury in the precipitate produced by Nessler's reagent is inexact.
M. A. W.

Two New Colour Reactions for Nitric Acid. C. REICHARD (*Chem. Zeit.*, 1906, 30, 790—791).—A drop of a solution supposed to contain a nitrate is mixed with a drop of a 5 per cent. solution of arbutin, and, after evaporating to dryness, the residue is moistened with a drop of sulphuric acid. The colour then changes to a deep permanent yellow. Free nitric acid should be neutralised with alkali hydroxide or ammonia before evaporating. Hydrochloric acid may be used instead of sulphuric acid. If the resulting yellow

solution is absorbed by a strip of filter paper, and a drop of potassium hydroxide solution added, a reddish-yellow spot is produced.

A still more delicate test for nitric acid is found in berberine hydrochloride. The best way to apply this test is to add to a drop of the nitric acid or nitrate solution a little berberine hydrochloride and then a drop of sulphuric acid, when a dark brownish-red coloration is observed. Hydrochloric acid produces the same effect on warming.

L. DE K.

Detection of Small Quantities of White Phosphorus in Presence of Large Quantities of Phosphorus Sesquisulphide.

LOUIS ARONSTEIN (*Chem. Centr.*, 1906, i, 1906; from *Chem. Weekblad*, 3, 283—287).—Either hydrogen (after passing through potassium permanganate solution and then sulphuric acid) or carbon dioxide (after passing successively through water and sulphuric acid) is mixed by means of a T-tube with dry air and the mixture passed over the phosphorus sesquisulphide to be examined for white phosphorus. If the latter is present, phosphorescence is observed when the gaseous mixture contains only a small proportion of air; this phosphorescence disappears if the proportion of air is increased, and reappears if it is lowered again. Pure phosphorus sesquisulphide only shows this behaviour at a temperature of above 80°. This method is sensitive to 0.2 per cent. of white phosphorus if the absolute amount is not less than 0.04 milligram. If the test is applied to material containing turpentine oil, alcohol, or other volatile substances, the phosphorescence is only observed after the gas has been passing for several minutes. The test is successful with material which has been kept for a week or longer.

T. H. P.

Estimation of Phosphoric Acid as Magnesium Pyrophosphate. B. SCHMITZ (*Zeit. anal. Chem.*, 1906, 45, 512—522).—A slight modification of the usual method, ensuring a pyrophosphate of theoretical composition.

The solution of the phosphate is mixed with a large excess of magnesia mixture acidified with hydrochloric acid and with a solution of ammonium chloride and heated to boiling. A 2½ per cent. solution of ammonia is now added slowly, while stirring vigorously, until the liquid is alkaline to phenolphthalein paper. When cold, about one-fifth of the bulk of strong ammonia is added, and after ten minutes the precipitate may be collected and burnt without previous drying. If a preliminary separation as phosphomolybdate is advisable, the yellow precipitate obtained as usual is washed with a 7 per cent. solution of ammonium nitrate and dissolved in a little ammonia, washing the beaker and filter with a 2½ per cent. ammonia solution. The bulk of the ammonia is now neutralised with hydrochloric acid, acidified magnesia mixture is added, and the whole is heated to boiling. After adding a drop of phenolphthalein, 2½ per cent. ammonia is added rapidly until the liquid becomes pink. When cold, about one-fifth of the bulk of ammonia is added and the precipitate is collected as directed previously.

L. DE K.

Estimation of the Amount of Arsenic in the Arsenic Mirror. JOHAN C. BERNTROP (*Chem. Centr.*, 1906, ii, 156—157; from *Chem. Weekblad*, 3, 315—322).—The author first describes the form of apparatus employed to evolve hydrogen arsenide from the material containing arsenic, and to deposit a mirror of arsenic on the walls of a narrow tube. The deposited arsenic is oxidised at about 60° by means of potassium dichromate and sulphuric acid, according to the equation

$5\text{K}_2\text{Cr}_2\text{O}_7 + 20\text{H}_2\text{SO}_4 + 6\text{As} = 5\text{K}_2\text{SO}_4 + 20\text{H}_2\text{O} + 5\text{Cr}_2(\text{SO}_4)_3 + 3\text{As}_2\text{O}_5$; the unaltered excess of dichromate is then estimated by means of potassium iodide and sodium thiosulphate solution. The amounts of arsenic dealt with by the author vary from about 0.0001 to 0.001 gram of arsenious oxide.

For legal purposes, it is important to isolate the arsenic from the liquid left after the titration. This can be done as follows: concentrated nitric acid is added and the iodine driven off by evaporating the solution until white vapours of sulphuric acid appear; diphenylamine is used to ensure that the nitric acid is also removed during this operation. The arsenic can then be identified in the mirror by sublimation, by its appearance, and by a microscopical examination.

T. H. P.

Estimation of Carbon Dioxide in Waters. GUSTAVE BRUHNS (*Zeit. anal. Chem.*, 1906, 45, 473—488).—An improved apparatus for estimating carbon dioxide in waters by the Pettenkofer process, whereby any error due to the action of atmospheric carbon dioxide during the filtration and titration is avoided, the liquid being covered with a layer of light petroleum.

Addition of ammonium chloride to waters containing magnesium leads often to inaccurate results. The magnesium should therefore be estimated and duly allowed for.

L. DE K.

Indirect Estimation of Small Quantities of Magnesium by Weighing as Phosphomolybdic Anhydride. GEORG BERJU (*Chem. Zeit.*, 1906, 30, 823—825. Compare this vol., ii, 250).—The magnesium ammonium phosphate, purified by redissolving and reprecipitating, is treated with molybdate solution, and the resulting yellow precipitate is converted with the usual precautions into phosphomolybdic anhydride.

L. DE K.

The Hydrolysis of Salts of Iron, Chromium, Tin, Cobalt, Nickel, and Zinc in the Presence of Iodides and Iodates. SETH E. MOODY (*Amer. J. Sci.*, 1906, [iv], 22, 176—184. Compare *Abstr.*, 1905, ii, 765).—Ferric and ferrous salts are hydrolysed by a mixture of iodide and iodate, and an equivalent quantity of iodine is liberated. The process, which can be used for the estimation of iron, is carried out by boiling the mixed solutions in a Voit flask in a current of hydrogen, the iodine carried over being collected and titrated with sodium thiosulphate. The reactions are represented by the equations $\text{Fe}_2(\text{SO}_4)_3 + 5\text{KI} + \text{KIO}_3 + 3\text{H}_2\text{O} = 2\text{Fe}(\text{OH})_3 + 3\text{K}_2\text{SO}_4 + 6\text{I}$; $3\text{FeSO}_4 + 5\text{KI} + \text{KIO}_3 + 3\text{H}_2\text{O} = 3\text{Fe}(\text{OH})_2 + 3\text{K}_2\text{SO}_4 + 6\text{I}$; $6\text{Fe}(\text{OH})_2 + \text{KIO}_3 +$

$3\text{H}_2\text{O} = \text{KI} + 6\text{Fe}(\text{OH})_3$. In the case of ferrous salts, the precipitated hydroxide is further converted into the ferric condition by the action of the excess of iodate. Chromium salts are hydrolysed similarly, and the chromium estimated either by weighing the precipitated hydroxide or titrating the liberated iodine. The reaction is also quantitative in the case of cobalt, nickel, and stannic salts, and takes place quite readily in the cold in the case of tin. Zinc salts are incompletely hydrolysed; the iodine liberated, whilst being very constant, is only 80.1 per cent. of the theoretical quantity. The precipitate is a basic salt, which contains 5Zn for SO_4 , and the reaction can be represented by the equation $15\text{ZnSO}_4 + 20\text{KI} + 4\text{KIO}_3 + 12\text{H}_2\text{O} = 3\text{Zn}_5(\text{OH})_8\text{SO}_4 + 12\text{K}_2\text{SO}_4 + 24\text{I}$.
H. M. D.

Separation of Ferric Iron from Manganese, Nickel, Cobalt, and Zinc by the Formate Process. W. FUNK (*Zeit. anal. Chem.*, 1906, 45, 489—504. Compare this vol., ii, 398).—The acid solution is mixed with 2 mols. of ammonium chloride for 1 atom of iron supposed to be present, and the whole is evaporated on the water-bath almost to dryness; the mass is broken up by means of a rod and the drying continued for a very short time. The residue is dissolved in water and mixed with solution of ammonium formate, about twice as much as is required theoretically. The liquid is now diluted copiously, but the amount of ammonium formate should not become less than 1/800. The solution is now heated until a precipitate begins to form, and the liquid is nearly neutralised by addition of very weak ammonia. After heating for a minute longer, the basic ferric formate is collected, washed with a very weak solution of ammonium formate, dried, ignited to oxide, and weighed.

The filtrate is evaporated with sulphuric acid, when the formic acid is readily and completely expelled; this fact renders the formic preferable to the acetate process. The metals may then be separated at once by the usual method.
L. DE K.

Analysis of Native Molybdenum Sulphide. ADOLPH GILBERT (*Zeit. öfentl. Chem.*, 1906, 12, 263—265).—About 1 gram of the finely powdered ore is placed in a porcelain boat and heated in a combustion tube for four hours. The contents of the boat are then boiled with fairly concentrated ammonia for about three hours, a little molybdic acid which volatilises on to the sides of the combustion tube being dissolved in ammonia and added to the main solution. The solution is filtered, the filtrate evaporated in a platinum basin, and the residue cautiously heated over a flame until constant in weight. The bottom of the basin should not be allowed to become more than dull red hot. The contents of the basin are next dissolved in ammonia, and a little insoluble residue, consisting mainly of silica, separated and deducted from the total weight of the molybdic acid. The first treatment of the roasted ore generally leaves a trace of molybdic acid in the residue. The latter is therefore fused with potassium and sodium carbonates, the fused mass heated with water and a little alcohol (to remove manganese), and filtered. The filtrate is acidified with hydrochloric acid, reduced with zinc, and titrated with permanganate solution.
W. P. S.

Iodometric Estimation of Vanadic Acid in Vanadium Ores. PAUL HETT and ADOLPH GILBERT (*Zeit. öffentl. Chem.*, 1906, 12, 265—266).—The method proposed is based on the reduction of vanadium pentoxide by potassium iodide in acid solution; iodine is liberated according to the equation: $V_2O_5 + 2HI = V_2O_4 + H_2O + I_2$, and is titrated in the usual manner. A weighed portion of the powdered ore is fused with sodium hydroxide, the fused mass is dissolved in water, and the solution filtered to remove any iron which may be present. The filtrate is then acidified with either hydrochloric or sulphuric acid, potassium iodide is added, and the liberated iodine titrated.

W. P. S.

Estimation of Tantalum by Marignac's Method. ARTHUR TIGHE (*J. Soc. Chem. Ind.*, 1906, 25, 681).—In estimating tantalum as the pentoxide by Marignac's method, the author experienced considerable difficulty in obtaining crystals of the double fluoride, K_2TaF_7 . The crystals appeared only when an amount of potassium hydrogen fluoride equal to twice the weight of the ore taken for the estimation was added to the solution of the mixed oxides of tantalum and niobium. It was also found that when the mixed oxides are dried in an air-oven they become almost insoluble in aqueous hydrofluoric acid, although they are readily soluble before drying. It is therefore necessary to determine their weight by a separate experiment.

W. P. S.

New Method for the Separation of Antimony and Tin. A. CZERWEK (*Zeit. anal. Chem.*, 1906, 45, 505—512).—0.5 gram of the alloy is dissolved at 40—50° in a mixture of 15 c.c. of nitric acid of sp. gr. 1.42, 15 c.c. of water, and 6 grams of tartaric acid. When dissolved, the liquid is heated to boiling and the tin completely precipitated by adding a slight excess of phosphoric acid of sp. gr. 1.3. The liquid is now diluted with boiling water to 300 c.c. and the tin phosphate is collected and washed with hot solution of ammonium nitrate. The filtrate containing the antimony is neutralised with ammonia mixed with excess of ammonium sulphide and then acidified with acetic acid. The antimonious sulphide is finally converted into the peroxide by treatment with fuming nitric acid with the usual precautions.

The tin phosphate is dissolved in warm ammonium sulphide, precipitated as sulphide by acidifying the cold strongly diluted solution with dilute sulphuric acid, and finally converted into oxide by nitric acid in the usual manner. Other metals, if present (such as copper and lead), will remain insoluble in the ammonium sulphide, and can be further examined.

L. DE K.

Estimation of Nitrogen in Nitrocellulose. MAX BUSCH (*Zeit. angew. Chem.*, 1906, 30, 1329).—The method is based on the complete conversion of the nitrogen into nitrate by the action of alkaline hydrogen peroxide and subsequent addition of sulphuric acid. About 0.2 gram of the sample is heated on the water-bath in a not too wide Erlenmeyer flask of 150 c.c. capacity with 5 c.c. of 30 per cent. sodium hydroxide and 10 c.c. of 3 per cent. hydrogen peroxide until the froth-

ing has subsided, and then boiled over the naked flame until dissolved. Another 40 c.c. of water and 10 c.c. of hydrogen peroxide are added, the liquid is heated to 50°, and by means of a pipette 40 c.c. of 5 per cent. sulphuric acid are delivered at the bottom of the flask. The liquid is now heated to 80°, and 12 c.c. of a 10 per cent. solution of "nitron" in 5 per cent. acetic acid are added, the mixture is allowed to cool and then placed in iced water for two hours. The precipitated nitrate is collected at the pump, the flask is washed with the filtrate, and the precipitate is then washed with iced water three or four times, using 10 c.c. of wash water in all.

The precipitate is dried at 110° for forty-five minutes and its weight calculated into nitrogen (compare Abstr., 1905, ii, 282).

L. DE K.

Estimation of Ammonia in Animal Tissues. ERICH GRAFE (*Zeit. physiol. Chem.*, 1906, 48, 300—314).—Fifty grams of the finely-divided tissue are mixed with 100 c.c. of concentrated sodium chloride solution, 50 c.c. of alcohol, and 100 c.c. of distilled water in the distillation flask, saturated sodium carbonate solution (50 c.c.) is run in, and the whole is distilled under reduced pressure, first at 25—28° and ultimately at 37—38°, in an apparatus similar to that used by Krüger and Reich (Abstr., 1903, ii, 688).

Parallel experiments gave concordant results, in the case of muscle agreeing to within 0.7 per cent. When magnesia is used to liberate the ammonia (Nencki and Zaleski, Abstr., 1901, ii, 688), the percentage of ammonia is much higher, and on redistillation further small amounts of ammonia are evolved, owing to the decomposition of labile nitrogenous compounds.

J. J. S.

Masking of Iodine in Presence of Saccharine Matters. P. GRÉLOT (*J. Pharm. Chim.*, 1906, [vi], 24, 154—161).—A series of experiments, illustrated by tables and curves, showing that sucrose, lactose, dextrose, and gum arabic absorb in the cold varying proportions of iodine, the amount depending on the concentration, and especially on the time of contact and the temperature. So long as there is still free iodine present, the iodine which has disappeared exists as hydriodic acid, but this is afterwards absorbed by the organic compound, forming an as yet unknown substance. In presence of free iodine the estimation of the total iodine is still possible by titrating in the usual manner after adding some potassium iodate, which liberates iodine in contact with hydriodic acid.

L. DE K.

Determination of the Yield of Formaldehyde in Various Methods of Liberating the Gas for the Disinfection of Rooms. DANIEL BASE (*J. Amer. Chem. Soc.*, 1906, 28, 964—993).—The author has determined the amounts of formaldehyde introduced into the atmosphere of a room by means of various methods of liberating the aldehyde. In the method of estimation employed, the air was drawn from the room, which contained 2000 cub. ft. of air, through tubes projecting midway between the ceiling and the floor, and through a series of three absorption tubes containing a solution of 6.6 grams of potass-

ium cyanide per litre, and two tubes containing silver nitrate solution to prevent loss of hydrogen cyanide and water respectively. At the conclusion of the experiment, the contents of the tubes were mixed, precipitated with an excess of silver nitrate, filtered, and titrated with thiocyanate solution. The potassium cyanide solution in the absorption tubes may be displaced by water (compare Trillat, *Abstr.*, 1905, i, 325).

On the basis of the results obtained, the methods of liberating formaldehyde for disinfecting purposes are discussed and placed in order of efficiency. G. Y.

Estimation of Small Quantities of Sugar in Urine. J. BLAISE (*Ann. Chim. anal.*, 1906, 11, 285—287).—Urines which contain but small amounts of dextrose give, when boiled with Fehling's solution, a yellowish-green precipitate which remains in suspension in the liquid and obscures the end-point of the titration. To overcome this difficulty it is recommended that the usual quantity of Fehling's solution taken for the estimation, namely, 10 c.c., should be boiled with the addition of 0.01 gram of dextrose and the titration then completed by running in the urine under examination. The precipitate of cuprous oxide formed by the added dextrose appears to have a considerable influence on the rapid settling of the precipitate produced by the sugar in the urine. A correction is, of course, made for the quantity of dextrose added. W. P. S.

New Reactions for Acetoacetic Acid. E. RIEGLER (*Chem. Centr.*, 1906, i, 1907; from *Münch. med. Woch.*, 53, 448—449).—The author discusses his own (*Abstr.*, 1903, ii, 112) and certain other methods for detecting acetoacetic acid in diabetic urine. T. H. P.

Assay of Commercial Tartaric Acid. P. CARLES (*Bull. Soc. chim.*, 1906, [iii], 35, 571—575).—In making the assay by the method already described (*Abstr.*, 1898, ii, 465, 545; this vol., ii, 313), the alkaline tartrate solution should be evaporated to 13—15 c.c., 3—4 c.c. of glacial acetic acid should be added after cooling, and the mixture should be shaken for ten minutes. Calcium phosphate has no influence on the results, but iron phosphate causes a loss of about 1 per cent. of the tartrate, and alumina increases this loss to 2 per cent. T. A. H.

Importance of the Determination of the Freezing Point in the Examination of Milk; Abnormal Milk. A. A. BONNEMA (*Chem. Centr.*, 1906, i, 1907—1908; from *Pharm. Weekblad*, 43, 434—444).—The mean freezing point of milk is -0.555° and is influenced by the presence of dissolved crystallisable substances. The average percentage composition of the milk of North Dutch or Frisian cows is: fat, 3; proteids, 3.5; lactose, 4.3; mineral matter, 0.7; and water, 88.5. The weight of water added per 100 parts of milk is given by $w = 0.555 \times 88.5/D - 88.5$, where D is the amount by which the freezing point of the milk differs from 0° . The influence of electrolytic and hydrolytic dissociation is, in

general, very small and may be obviated entirely by calculating in percentages by volume. The rise which occurs in the freezing point of milk soon after milking is due to the formation by bacteria of ammonia, by which part of the dissolved phosphate is precipitated, whilst the subsequent rise of freezing point is caused by the formation, also by bacteria, of lactic acid, which partially dissolves the insoluble phosphate.

The soluble phosphates may be titrated with $N/4$ sodium hydroxide solution, using phenolphthalein as indicator. Sodium dihydrogen phosphate, NaH_2PO_4 , which has an acid reaction, is thus changed into the neutral disodium salt, Na_2HPO_4 , and the latter is converted by the slightest excess of sodium hydroxide into the alkaline trisodium phosphate.

Boiling the milk nearly always produces an elevation of the freezing point. Shortly after calving, the milk has a high degree of acidity, namely, 4.5, is rich in phosphates and poor in chlorides; hence, when the milk is boiled, its freezing point is lowered, because the hydrolytic dissociation of the secondary phosphates increases. Milk from cows which have been giving milk for a long time contains, on the other hand, only small proportions of tertiary phosphates, but has a high chlorine-content, which varies from 0.068—0.140 gram per 100 c.c., the mean being 0.108 gram.

T. H. P.

Presence and Detection of Cyanogen in Java, Burma, and Haricot Beans. ROBERT R. TATLOCK and ROBERT T. THOMSON (*Analyst*, 1906, 31, 249—252).—Several specimens of Java beans examined were found to contain from 0.027 to 0.137 per cent. of hydrocyanic acid, the acid existing in the beans in the form of a glucoside resembling amygdalin. The colour of the beans is no indication of the quantity of hydrocyanic acid they may contain, and the kernel contains, apparently, about ten times as much of the glucoside as the husk. Three samples of ordinary haricot beans yielded from 0.001 to 0.009 per cent. of hydrocyanic acid, whilst 0.005 per cent. of the latter was obtained from a sample of Burma beans. A large proportion of the cyanogen compound and the whole of the enzyme was found to be destroyed by boiling the beans with water.

W. P. S.

Analytical Reactions of Coniine. EMILIO GABUTTI (*Chem. Centr.*, 1906, ii, 74; from *Boll. Chim. Farm.*, 45, 289—290).—When a very dilute sodium nitroprusside solution is added to a very dilute solution of coniine, an intense red coloration is formed slowly, more rapidly on shaking, and gradually changes into yellow; boiling the liquid causes the disappearance of the colour, which reappears on cooling. In alcoholic solutions, the reaction does not take place, and with ethereal solutions only the lower aqueous layer is coloured. Addition of acids, especially concentrated ones, destroys the red colour, and on further addition of an alkali hydroxide, but not ammonia or alkali carbonate, the yellow coloration appears. A small quantity of an aldehyde changes the red colour to violet, a larger quantity to blue, whilst excess of the aldehyde causes

a disappearance of the colour. If the liquid containing either excess or an insufficient quantity of the aldehyde is evaporated on the water-bath, a characteristic blue ring appears. The violet or blue colour disappears on boiling the solution without reappearing when the latter cools, and changes rapidly into green after a time, and is then changed gradually into yellow by alkali hydrogen sulphite, into pink by mineral acid, and into blue by acetic acid.

Sodium nitroprusside does not give these colour reactions with piperidine, piperazine, aliphatic amines, or nicotine. T. H. P.

Reaction for Indole. K. KONTO (*Zeit. physiol. Chem.*, 1906, 48, 185—186).—A dilute solution of indole, even 1 in 500,000 gives a violet-red coloration when shaken with pure concentrated sulphuric acid and a little 4 per cent. solution of formaldehyde. Small amounts of scatole do not interfere with the reaction.

By means of this reaction indole has been detected in the decomposition products of proteids and in fæces, after distillation in steam and removal of ammonia. J. J. S.

Examination of Bleached Flour. ROSCOE H. SHAW (*J. Amer. Chem. Soc.*, 1906, 28, 687—688).—The process is devised for the identification of flour bleached by the higher oxides of nitrogen.

About 1 kilogram of the sample is boiled for four hours with strong alcohol in a reflux apparatus. When cold, the liquid is filtered and the filtrate plus one washing is evaporated nearly to dryness. The residue is extracted with a mixture of equal parts of alcohol and ether, and this is evaporated in a small porcelain dish, care being taken to spread the mass well over the sides. The residue is now tested for nitrate by means of a drop of sulphuric acid and a solution of diphenylamine in dilute sulphuric acid. The investigation is being continued.

L. DE K.

Note on Soil Analysis. MATS WEIBULL (*Chem. Zeit.*, 1906, 30, 722).—The author attaches great importance to the amount of alumina soluble in strong sulphuric acid, as it is a measure of the amount of kaolin and zeolites present in the soils.

The amount of potassium soluble in hydrochloric acid of sp. gr. 1.1 is not an exact criterion of the suitability of the soil for barley growing. A case is mentioned where a soil with a potassium content of only 0.08 per cent. gave a bad barley crop, as might have been expected. However, after being manured with lime the same soil proved satisfactory.

L. DE K.

General and Physical Chemistry.

Determinations of Wave-length from Spectra obtained at the Total Solar Eclipses of 1900, 1901, and 1905. F. W. DYSON (*Phil. Trans.*, 1906, 206, A, 403—452).—The wave-lengths of the lines present in the spectrum of the chromosphere are given in tabular form, and opposite are placed the wave-lengths of terrestrial elements with which they may probably be identified. The great majority of the stronger lines correspond with the strong spark-lines of titanium, chromium, scandium, yttrium, iron, manganese, and zirconium, as measured by Exner and Haschek. Indications of the presence of many of the terrestrial metals have been obtained, although in many cases the lines are faint. The carbon lines are shown, but not very strongly. The helium lines are strongly marked; those of parhelium are doubtful, and there is no evidence of the existence of argon, xenon, neon, or krypton in the chromosphere.

The wave-lengths of some of the lines present in the spectrum of the corona are also tabulated. G. S.

Absorption Spectra of the Rare Earths. ABRAHAM LANGLET (*Zeit. physikal. Chem.*, 1906, 56, 624—644. Compare Abstr., 1902, ii, 189; also Liveing, Abstr., 1900, ii, 517; Purvis, Abstr., 1904, ii, 4).—A critical review of the work already done in this field and an account of the author's own experiments on the absorption spectra of solutions of praseodymium and erbium salts. He finds that the aqueous solutions of different salts of the same earth, if they are sufficiently dilute, yield identical spectra, and that the spectrum of a sufficiently dilute solution is therefore to be regarded as an ion spectrum. Everything which causes a repression of the electrolytic dissociation causes also corresponding changes in the absorption spectrum, changes, however, which are different for the different salts. The presence of colourless earths in large excess represses the dissociation and causes changes in the absorption spectra, which, especially in the case of nitrates, may affect the relative intensity of the bands.

J. C. P.

Ultra-violet Spectrum of Ytterbium. Sir WILLIAM CROOKES (*Proc. Roy. Soc.*, 1906, 78, A, 154—156).—The samples of ytterbia used in the experiments were prepared by different methods; a specimen prepared by Urbain from the gadolinite earths by fractional crystallisation of the ethyl sulphates and subsequent separation by partial decomposition of the nitrates by heat was largely employed. The spark spectrum from a strong solution of the nitrate between platinum poles was photographed; the dominant lines are at 3289.5 and 3694.4. The results showed that the specimen was not quite pure, containing traces of thulium, copper, and calcium. G. S.

Phosphorescence of Nitrogen and Sodium. K. VON MOSENGEIL (*Ann. Physik*, 1906, [iv], 20, 833—836).—Lewis considered that the phosphorescence of nitrogen is due to the presence of small quantities of oxygen, inasmuch as it disappears on the introduction of sodium. The author finds, however, that the sodium itself is the cause of the prevention of the phosphorescence, which is not due to the presence of oxygen. The sodium itself, however, gives rise to phosphorescence (*Abstr.*, 1900, ii, 702). L. M. J.

Relation between Fluorescence and the Chemical Constitution of Organic Substances. LUIGI FRANCESCONI and GUIDO BARGELLINI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 184—191).—A very delicate method of detecting fluorescence has been devised which consists in concentrating by means of a lens a cone of sunlight on the solution of the substance contained in a test-tube in a darkened box; on examining the solution from above, the illuminated portion appears of a different colour from that of the rest of the solution. With this arrangement, about 500 different substances have been examined, under different conditions of concentration and temperature, in neutral, acid, and alkaline solution. Many substances which to the ordinary eye do not appear fluorescent, with this arrangement are seen to fluoresce distinctly, whilst substances ordinarily feebly fluorescent show a strongly defined cone of colour. The striking fact is established that fluorescence is lacking in the aliphatic class, and in alicyclic compounds in which the fatty character dominates the aromatic. The conclusion is drawn that fluorescence is potential in all aromatic compounds; certain groups, however, increase the fluorescence (for example, the groups, NH_2 , OH , CO_2H), whilst others diminish it (NO_2 , Cl , Br , &c.). The former groups are termed *auxofluors*, the latter *bathofluors* (compare *Abstr.*, 1903, i, 34; 1904, i, 168). Tables are added showing that the group NH_2 (or NHMe , NMe_2) exercises very great influence in increasing fluorescence; the same holds true, in a lesser degree, of the groups OH , CN , CO_2H (or CO_2Et). The group $-\text{CH}:\text{CH}$ is an auxofluor, but the group $-\text{N}:\text{N}-$ is one of the strongest of the bathofluors. The acetyl and benzoyl groups act as bathofluors when present as substituents in a hydroxyl or amino-group. The sulphonic group, SO_3H , seems to be a feeble auxofluor, but its influence is not yet well established. W. A. D.

Fluorescence, Magnetic Rotation, and Temperature Emission Spectra of Iodine Vapour. ROBERT W. WOOD (*Phil. Mag.*, 1906, [vi], 12, 329—336).—The fluorescence of iodine is best seen in a moderately high vacuum. If a glass bulb with a few flakes of iodine is exhausted and sealed, a yellowish-green fluorescence appears if a beam of sun- or arc-light is focussed to the centre of the bulb. If the bulb contains air, no fluorescence occurs until the pressure is reduced to about 15 cm.; with hydrogen it appears at about 30 cm. If the bulb is warmed, the fluorescence appears at higher pressures, and the author considers that this, and some other analogous phenomena, may be best explained by the assumption of a kind of gaseous solution—that is, that air at 15 cm. pressure is able to dissolve all the iodine which vaporises at the ordinary temperature, but

that by rise of temperature and consequent increased pressure of iodine some of the iodine remains undissolved. The fluorescence spectrum is reproduced in the paper, and consists of a number of bands extending from the orange-red far down into the greenish-blue. To obtain the magnetic rotation spectrum, a small, exhausted bulb containing iodine was placed in a brass tube between the poles of a magnet. Parallel arc-light was passed through a Nicol prism, the bulb, and a second Nicol prism set for extinction. When the magnet was excited, an intense blaze of emerald-green light was obtained. The spectrum is reproduced; none of the magnetic lines appear to be doubled, and in many places the spectrum is complementary to the absorption spectrum. When heated at 700° , iodine vapour gives a highly luminous red cloud. The spectrum of this in a bulb appeared almost continuous, but when obtained from a capillary tube, it was found to give a band spectrum closely resembling the fluorescence spectrum, but with the bands displaced towards the red.

L. M. J.

Theory of Optical Activity. THOMAS S. PATTERSON (*Zeit. physikal. Chem.*, 1906, **56**, 366—369. Compare Winther, this vol., ii, 320).—The author points out that his views on several points connected with optical activity have not been accurately stated by Winther.

J. C. P.

Chemical and Electrical Changes induced by Ultra-violet Light. Sir WILLIAM RAMSAY and JAMES F. SPENCER (*Phil. Mag.*, 1906, [vi], **12**, 397—418).—A number of experiments are described which are in accord with the hypothesis given in the introduction to the paper, namely, that positive ions are atoms of elements which have lost one or more electrons, and negative ions those which have gained such electron. Thus sodium combined with chlorine and dissolved in water forms sodium ions and chlorine ions, that is, the electron at first attached to the sodium becomes, by the union, more closely connected to the chlorine and remains with it in solution. The current of a simple cell is explained thus: the zinc plate consists of zinc with electrons, the acid of hydrogen and of chlorine with its electron. When zinc goes into solution, the displacement of electrons occurs, and these electrons pass through the zinc plate and copper wire to the copper plate, where they combine with ionic hydrogen to form gaseous hydrogen. The electrons appear to be associated with matter in three ways: (1) as a surface film removed by friction (electrification); (2) associated with elements to form ions; (3) associated with one kind of matter to form another kind of matter, so that if the electron is lost without leaving the matter a positive ion, the matter disintegrates into atoms of lower weight. Many metals lose their electrons under the influence of ultra-violet light, and the phenomenon is investigated. A large number of metals was investigated, and in general the rates of discharge of the element, that is, the rates of emission of electrons, are in the same order as their electro-potentials. Some exceptions occur, for example, manganese, iron, chromium, gold, nickel, and cobalt, and it is noteworthy that these readily take up the passive

form. As sodium, even in the dark, emits corpuscles, the ultra-violet light probably acts as an accelerator of the disintegration. Experiments were next made with compounds (sulphides and iodides), and they indicated that there was an emission of corpuscles from compounds as from metals. The *E.M.F.* of certain cells when one element is exposed to light is readily explained by the hypothesis, and it was shown that cells with similar electrodes of gold, copper, and cadmium in all cases gave an *E.M.F.* when one electrode was exposed to ultra-violet light. The firing of metals when exposed to ultra-violet light was fully examined for magnesium, aluminium, zinc, and tin. The curves give a number of breaks corresponding with the valencies, and the authors explain this by the assumption of "metallic corpuscles," as distinct from the ordinary electrons, corresponding with the valencies. The splitting off of electrons proceeds at a decreasing rate until a point is reached where the first "metallic corpuscle" is emitted and so on. When the last metallic corpuscle is expelled, the further expulsion of electrons at a decreasing rate indicates the further disintegration of the metal.

L. M. J.

Radioactivity of Thermal Springs in Aachen. N. SAHLBOM and F. WILLY HINRICHSSEN (*Ber.*, 1906, 39, 2607—2608).—Various thermal springs in Aachen were found by the authors to be feebly radioactive.

A. MCK.

Distribution of Radium in the Earth's Crust. II. ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1906, 78, A, 150—153. Compare this vol., ii, 411).—It has been shown that igneous rocks contain on an average 5×10^{-12} grams of radium per c.c. The author has now carried out a series of experiments with typical sedimentary deposits, including samples of chalk, sandstone, clay-slate, &c., and finds $0.25 - 5.8 \times 10^{-12}$ grams of radium per gram, so that the average radium content of sedimentary deposits does not differ appreciably from that of igneous rocks.

A deposit from the Bath springs yielded 828×10^{-12} grams of radium per gram, and was thus 100 times as rich as any rock; a sample of sea-salt contained 0.15×10^{-12} grams, and a sample of Cambridge tap-water a quantity of emanation corresponding with 0.78×10^{-12} grams of radium per gram.

Samples of rock-forming minerals from various parts of the world have been examined. Certain accessory minerals, such as zircon ($75 - 865 \times 10^{-12}$ grams per gram), sphene, and apatite ($11 - 30 \times 10^{-12}$ grams per gram), are rich in radium; hornblende, micas, and feldspars contain much less, whilst in a specimen of quartz none could be detected. As these results were not considered conclusive, owing more particularly to want of knowledge of the proportions in which the various minerals occur, a specimen of Cornish granite was separated into its constituents and investigated. The light portion (quartz and feldspar) contained 3.85×10^{-12} grams, the heavy portion 5.29×10^{-12} grams of radium per gram, so that the latter, although only constituting about one-eighth of the rock, contained considerably more than half the radium.

The additional data now available show no cause for altering the estimate of the age of the earth previously arrived at (*loc. cit.*).

G. S.

The Production of Helium from Radium. Sir WILLIAM CROOKES (*Chem. News*, 1906, 94, 144).—A small vacuum tube was made with platinum electrodes, the ends being curled into loops in which were fused beads of radium bromide. After exhaustion a 1" spark from an induction coil was passed through. Much carbon dioxide was evolved and the tube again exhausted. The spark was again passed and more carbon dioxide was evolved and removed. No helium could be detected. After four months the tube was again examined and the helium line (5875·9) was plainly visible. The green line of parhelium was also seen, but it was too faint to measure.

L. M. J.

Conductivity of Aqueous Solutions of Radium Bromide. FRIEDRICH KOHLRAUSCH and FRITZ HENNING (*Ann. Physik*, [iv], 20, 96—107. Compare Abstr., 1904, ii, 700).—The authors have determined the conductivities of solutions of radium bromide ranging in strength from 1/12000 to 1/20 equivalent. The temperature-coefficient of the conductivity is normal and diminishes as the concentration increases. No alteration of the conductivity with time, other than might be due to a slight absorption by the platinised platinum electrode, was observed. Platinum electrodes which have been in contact with a $N/20$ solution of radium bromide remain strongly radioactive after some years. The skin is very sensitive even to a 0·0001-normal solution of the salt.

Taking Runge and Precht's value for the atomic weight of radium, namely, 258, the mobility of the ions of radium becomes abnormally high, and in dilute solutions radium bromide would be the best conducting salt. The temperature-coefficient, also 0·0237, calculated from this high value for the atomic weight, would fall considerably outside the curve.

T. H. P.

Action of Becquerel Rays on Water. FRIEDRICH KOHLRAUSCH (*Ann. Physik*, [iv], 20, 87—95. Compare Abstr., 1904, ii, 692).—The change in conductivity of water produced by the passage of Becquerel rays is as small as that caused by ordinary light rays, that is, it is less than 0·1 per cent.

The water used by the author had a conductivity of 1×10^{-6} , so that it conducted thirty times as well as pure water. Using two similar vessels of water, one subjected to the action of Becquerel rays and the other not, it was found that the conductivity increased more rapidly in the former than in the latter; the increase diminished with lapse of time. The absolute increase of conductivity was but minimal, and can be explained by the presence of 1/800 mg. of salt, which becomes dissolved in the 25 c.c. of water used during the fourteen days over which the experiment extended. A current of air, passed over a radium-cell and then through the water, did not cause an increase in

the conductivity. The temperature-coefficient of the water subjected to the Becquerel rays is normal (0.0250 at 18°).

The probability is that the passage of the rays causes a slightly increased quantity of the glass to become dissolved in the water. The formation of fresh ions in the water is unlikely. T. H. P.

Ionisation Ranges of the α -Rays of Actinium. OSKAR HAHN (*Phil. Mag.*, 1906, [vi], 12, 244—254).—The apparatus used and the method of work were similar to those employed by the author in the case of thorium (this vol., ii, 416, 594), and by Bragg and Kleeman for radium products (*Abstr.*, 1905, ii, 5). The ranges of the α -particles for the various radioactive products are compared in the adjoined table:

Product.	Range.	Product.	Range.	Product.	Range.
Radioactinium....	4.8 cm.	Radiothorium ...	3.9 cm.	Radium	3.50 cm.
Actinium X.....	6.55 „	Thorium X	5.7 „	Emanation ...	4.33 „
Emanation	5.8 „	Emanation	5.5 „	Radium A	4.83 „
Actinium B.....	5.5 „	Thorium B	5.0 „	Radium C	7.06 „
		Thorium C	8.6 „	Radium F	3.86 „

It is shown in the course of the paper that the ionisation curves afford a good criterion for the determination of the particular α -ray products which are present. L. M. J.

Origin of the β -Rays emitted by Thorium and Actinium. MAX LEVIN (*Phil. Mag.*, 1906, [vi], 12, 177—188).—Thorium X was separated from thorium by precipitation by ammonia and the solution of thorium X dried on a platinum dish and heated in the blowpipe to remove the active deposit. Both α and β activity were measured when cold. The β activity was only 3.5 per cent. of the maximum activity attained one day later; the α activity was about 60 per cent. of its maximum. Both decay curves are very similar, decreasing exponentially to half value in about four days. If the rays are emitted equally by thorium X, emanation, thorium A, and thorium B, then the initial value should be about 50 per cent. of the total. The experiments show that, allowing for the decay of the thorium X, this is the case for the α -rays, but that the initial percentage of β activity is only 2.6 per cent., so that the transformation of thorium X into emanation is accompanied only by emission of α -rays. Similar experiments with thorium freed from thorium X and the later products indicate that neither thorium nor radiothorium emits β -rays. In the case of actinium X from which the active deposit had been removed, the β activity was about 3 per cent. and the α activity about two-thirds of the total maximum. Actinium X, therefore, emits no β -rays. The author considers that the contrary view of Godlewski (*Abstr.*, 1905, ii, 497) is due to the incomplete removal by the latter of the active deposit. Godlewski also found that actinium freed from actinium X showed little α activity whilst the author could not reduce this α activity below about 28 per cent. The cause of this discrepancy was found to be due to the substance radioactinium obtained by Hahn during the progress of the experiments, actinium itself being rayless (this vol., ii,

323). The author comments on the fact that, in the case of radium, thorium, and actinium, the β -ray is only emitted in the final change, and considers that this is probably of theoretical importance.

L. M. J.

Mass and Velocity of the α -Particles expelled from Radium and Actinium. ERNEST RUTHERFORD (*Phil. Mag.*, 1906, [vi], 12, 348—371).—The author has previously found the values $e/m = 6 \times 10^3$, and the highest velocity of the α -particle $= 2.5 \times 10^9$ cm./sec. Des Coudres found $e/m = 6.3 \times 10^3$, and the average velocity 1.65×10^9 cm./sec., whilst Mackenzie obtained the values 4.6×10^3 and 1.37×10^9 . The question is made complex by the fact that the α -particles come from four different α -ray products with different ionisation ranges and different projection velocities. In the present investigation homogeneous α -rays were employed by means of a small wire made active by exposure to radium emanation, which, after fifteen minutes, emits only radium C α -particles. The method and theory of the experiments are explained and the results and calculations recorded. The values finally obtained are $e/m = 5.07 \times 10^3$ and $v = 2.06 \times 10^9$, these results being considered accurate to about 2 per cent. Experiments were next made to test whether the value of e/m varies with the passage of the α -particle through matter. The values found after passage through mica screens equivalent to 3.5 cm. and 6.5 cm. of air were 5.07×10^3 and 4.8×10^3 respectively, and hence indicate that the ratio is not altered. The α -particles from radium A were obtained by the use of a number of active wires, each being employed for only a short period after its exposure to the emanation. The values obtained were 5.6×10^3 and 1.22×10^9 , but the experimental errors (greater than in the previous case) tend to give too high a value for e/m , and the author hence concludes that the α -particles from radium A and radium C have the same mass and differ only in initial velocity. The radium F α -particle was obtained by the use of a bismuth rod coated with radiotellurium, and values $e/m = 5.3 \times 10^3$ and $v = 1.73 \times 10^9$ were obtained; for actinium, $e/m = 4.7 \times 10^3$ and $v = 1.21 \times 10^9$. These results indicate that the α -particles expelled from the different radio-elements have the same mass in all cases, and that uranium, radium, actinium, and thorium (see succeeding abstract) have a common product of transformation. The value obtained for e/m is about one-half of that of the hydrogen atom. This may be explained on the assumption that the α -particle is (1) a molecule of hydrogen carrying the ionic charge, (2) a helium atom carrying twice the ionic charge, or (3) one-half of the helium atom carrying the ionic charge. Of these, (1) is evidently improbable, and the other two hypotheses are briefly discussed. From the quantity of contained helium the age of two radioactive minerals is calculated, being in each case about 400 million years. The energy and heating effects of the α -particles are calculated, the results being in good accord with observed values.

L. M. J.

Mass of the α -Particles from Thorium. ERNEST RUTHERFORD and OSKAR HAHN (*Phil. Mag.*, 1906, [vi], 12, 371—378).—The apparatus employed was that used by Rutherford in similar work on

radium (preceding abstract). The values obtained were $e/m = 5.6 \times 10^8$ and $v = 1.98 \times 10^9$. The experimental errors tend to give too high a value for e/m , so that the value may be regarded as in good accord with that obtained for other α -particles.

L. M. J.

Recombination of Ions made by α -, β -, γ -, and X-Rays. R. D. KLEEMAN (*Phil. Mag.*, 1906, [vi], 12, 273—297).—The current through a gas ionised by α -rays is unsaturated at low *E.M.F.*'s, and this has been ascribed to some of the ions being only partially separated from the parent molecule, so that in the absence of a strong electric field reunion occurs. This is termed *initial*, as distinct from *general*, recombination. In the case of air ionised by α -uranium rays, the lack of saturation at 8 volts per cm. was 22 per cent., whereas the general recombination was only 1/1400. In the case of X-rays, whether primary or secondary, the lack of saturation is small and initial recombination is almost absent, that is, the negative ion is separated almost completely from the parent molecule. Experiments were also made with mixtures of air and various vapours, chloroform, carbon tetrachloride, &c. In all these also, the lack of saturation for the α -uranium rays was great, but was small for the X-rays. These results probably indicate that the velocity of the electron ejected by ionisation by the α -particle is considerably less than its velocity when ejected by X-rays. The β - and γ -rays of uranium were also investigated, and, as in the case of X-rays, the initial recombination is small. For a mixture of α - and γ -rays the initial recombination was found to be that due to the separate effects. As the initial recombination is still small after passage of the β -rays through a thickness of 0.7 mm. aluminium, it is probable that the rays suffer but little decrease of velocity by the passage. Experiments with α -polonium rays showed that the lack of saturation increased with decrease of velocity of the α -particle; the velocity of the electron therefore probably decreases with that of the α -particle.

L. M. J.

Coefficient of Absorption of β -Rays from Uranium. J. ARNOLD CROWTHER (*Phil. Mag.*, 1906, [vi], 12, 379—392).—The intensity of radiation of initial intensity I_0 after passing through a thickness δ of material is given by the equation $I = I_0 e^{-\lambda \delta}$, where λ is the coefficient of absorption. If the absorption is due to the collision of the electron with the corpuscles forming the atom, and if the number of corpuscles in the atom is proportional to the atomic weight, then, if the stopping power of the corpuscle is the same for all substances, it follows simply that the coefficient of absorption should be proportional to the density, that $\lambda/\rho = \text{constant}$. The author's experiments were made to determine whether or not this is the case. He finds the values of λ/ρ vary from 4.4 to 10.8 in the thirty-one elements examined, and that if the values of λ/ρ be plotted against atomic weights a periodic curve is obtained in which elements of the same group occur in similar parts of the curves. The value λ/ρ increases with atomic weight in the case of allied elements. Allotropic forms of the same element, however, give identical values. The value of λ/ρ for compounds was found to be an additive quantity, so that the absorptive power of the element is not altered when it enters into combination.

L. M. J.

New Methods of Separating Uranium X from Uranium.

RICHARD B. MOORE and HERMAN SCHLUNDT (*Phil. Mag.*, 1906, [vi], 12, 393—396).—If uranium nitrate is dissolved in acetone, a small residue is left which is far more active than the salt in the filtrate. If moist ferric hydroxide is then stirred into the filtrate, the uranium nitrate is practically freed from uranium X; the ratio of the amounts of uranium X in the residue and in the ferric hydroxide, however, varies with the sample of uranium nitrate used. The following liquids also may be used in place of acetone: methyl acetate, ethyl acetate, methyl, ethyl and amyl alcohols, and ethyl acetoacetate. In all cases the uranium X so obtained was found to emit α - as well as β -rays.

L. M. J.

Production of Secondary Rays by α -Rays from Polonium.

W. H. LOGEMAN (*Proc. Roy. Soc.*, 1906, 78, A, 212—217).—Since α -rays are absorbed by a solid, according to the same law as by a gas, it is to be expected that the atoms of a solid are ionised in the same manner as those of a gas, and that slowly moving negative rays will be emitted when the α -rays enter or leave a solid. Experiments with the α -rays from polonium indicate that this takes place when the rays are allowed to fall on an aluminium or copper plate in a tube exhausted to a pressure of about 0.001 mm. of mercury. The source of the α -rays was a copper disc covered with a thin layer of polonium and placed parallel to the receiving plate at a distance of 5 or 10 mm. Measurements of the leakage current between the plates were made with and without the superposition of an electrostatic or a magnetic field. When unacted on by electrostatic or magnetic forces, polonium gives off a larger amount of negative than of positive rays. With a gradually increasing electrostatic field, more and more of the slowly moving negative (δ) rays are stopped, and the charge carried by the α -rays becomes increasingly predominant. A difference of potential of about 10 volts between the plates suffices to stop completely the δ -rays, and the same effect is produced by a magnetic field of about 100 C.G.S. units.

The limiting value of the positive current from the polonium plate when the δ -rays are stopped by a magnetic field is, however, only about one-fifth of that obtained when the rays are stopped by an electric field. To explain this fact, the author supposes that when the difference of potential between the plates is greater than 10 volts (the polonium plate being positively charged), the current consists of two parts: (1) a stream of α -particles from the polonium; (2) a stream of negative particles from the bombarded copper or aluminium plate towards the polonium. These negative particles, as well as the δ -rays emitted by the polonium, are stopped by the magnetic field.

H. M. D.

Polonium and Radiotellurium.

WILLY MARCKWALD (*Chem. Centr.*, 1906, ii, 412—413; from *Physikal. Zeit.*, 1906, 7, 369—370. Compare Abstr., 1905, ii, 623).—The author points out that his radiotellurium is a well-defined, chemically pure substance, and that it is one thousand times more active than Madame Curie's polonium, which

has been shown to be a mixture. He nevertheless advocates the use of the name polonium in future to designate his radiotellurium.

P. H.

Phenomena Observed in Crookes' Tubes. N. T. BACON (*Amer. J. Sci.*, 1906, [iv], 22, 310—312).—The phenomena observed in connection with the discharge in Crookes' tubes are discussed. The gradual attenuation of the discharge, which is attributed to absorption of the residual gas, is supposed to be due to the imperfect elasticity of the solid state of aggregation. The emission of rays is supposed to be due to a resolution of atoms into electrons under the influence of the discharge.

H. M. D.

Photoelectric Behaviour of Anthracene. ALFREDO POCHETTINO (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 171—179. Compare this vol., ii, 417).—Measurements are described of the photoelectric activity of anthracene which show that its magnitude is nearly the same as that of zinc. The decay of the photoelectric effect with time is probably not due to the conversion of anthracene into dianthracene as previously supposed (*loc. cit.*), because of the slowness of the latter change as compared with the rate of decay of the photoelectric effect. The decay is observed only with the thicker films of anthracene; with a film 1/50 mm. in thickness little change occurs in the activity. Curves are given showing the decay of the photoelectric effect with layers 0.5 mm., 1 mm., and 3 mm. in thickness. The decay is attributed to the high dielectric qualities of anthracene, which, after ionising the air in its neighbourhood, gets superficially covered with a positive charge which prevents the current indicating the photoelectric effect from passing. This view is supported by the fact that the "fatigued" anthracene is restored in a few minutes to its original activity by subjecting it to the discharging action of the rays emitted by radium.

W. A. D.

Theory of Electromotive Force in Polyphase and Non-aqueous One-phase Systems. EMIL ABEL (*Zeit. physikal. Chem.*, 1906, 56, 612—623).—A theoretical paper.

J. C. P.

Ionic Conductivities at 25°. PHILIP BLACKMAN (*Chem. News*, 1906, 94, 176. Compare this vol., ii, 647).—The author has calculated the conductivity of a number of ions according to the method described by him, and has found that the maximum conductivity is attained at a dilution $v=512$.

P. H.

Conductivity of Concentrated Aqueous Solutions of Electrolytes. JOHN GIBSON (*Proc. Roy. Soc. Edin.*, 1906, 26, 234—237).—If the concentration of a solution is expressed in gram-equivalents per unit mass instead of per unit volume, K being the specific conductivity ($\text{ohm}^{-1}, \text{cm}^{-1}$), γ the concentration in gram-equivalents per gram, and $\Lambda_\mu = K/\gamma$, the relationship between Λ_μ and γ can be very closely expressed by the equation $\Lambda_\mu = a + b\gamma$ over very considerable ranges of concentration. For solutions of

strong acids, bases, and salts, the range of validity extends from about 0.5 to about 7.0 gram-equivalents per kilogram. Within these limits the connection between κ and γ may be written $\kappa = a\gamma + b\gamma^2$, which is the equation of a parabola with a maximum value of κ corresponding to $\gamma = -a/2b$. At still higher concentrations the relation between Λ_μ and γ ceases to be linear. If, however, the electrolyte is sufficiently soluble to give a solution of maximum specific conductivity, the maximum always falls within the range of concentration for which the linear relationship holds. The adoption of the unit of mass instead of the unit of volume does not in any way affect the numerical statement of the regularities established in the case of dilute solutions.

H. M. D.

Experiment to Demonstrate the Non-validity of the Tension Law for Electrolytes. FRIEDRICH DOLEZALEK and FRIEDRICH KRÜGER (*Zeit. Elektrochem.*, 1906, 12, 669—670).—Into a ring-shaped glass vessel, solutions of sulphuric acid (35 per cent.), sodium acetate (30 per cent.), and lithium chloride (20 per cent.) are placed so that they do not mix. The combination gives an *E.M.F.* of about 0.065 volt, and produces a current flowing round the ring. The existence of the current is shown by the deflection of an astatic combination of magnets suspended at the centre of the ring.

T. E.

Theory of Amphoteric Electrolytes. JAMES WALKER (*Zeit. physikal. Chem.*, 1906, 56, 575—576. Compare Abstr., 1904, ii, 309; 1905, ii, 138).—A criticism of Lundén's recent paper (this vol., ii, 265).

J. C. P.

Electrolytic-Gas Voltameters with Nickel Electrodes and the Formation of Nickel Peroxide. HANS RIESENFELD (*Zeit. Elektrochem.*, 1906, 12, 621—623).—Voltameters were set up with nickel electrodes in pure sodium hydroxide solution (15 per cent.). These were compared with voltameters with platinum electrodes and also with silver and copper voltameters. In all cases the nickel electrodes gave too little gas. The reason was discovered in the formation of nickel peroxide on the anode, owing to dissolution of nickel hydroxide in the solution of sodium hydroxide and its subsequent oxidation at the anode.

T. E.

Electrochemistry of the Iodine-Oxygen Compounds. ERICH BRUNNER (*Zeit. physikal. Chem.*, 1906, 56, 321—347).—The solutions examined were placed in a cell between two platinum electrodes and were kept stirred. The smaller of the two electrodes was taken as an "observation electrode," and while a measured current was passing through the cell the polarisation *E.M.F.* at the "observation electrode" was determined with the aid of an auxiliary electrode. In the curves obtained by plotting the current against the polarisation *E.M.F.* there are frequently portions which are nearly horizontal, that is, there are short ranges of the polarisation *E.M.F.* for which the current is almost constant. The currents for such *E.M.F.* ranges are called by the author "limit" currents ("Grenz-

ströme"), and from these the corresponding process taking place at the electrode may be deduced.

When the solution examined is an acidified solution of iodine in potassium iodide, so dilute that no solid iodine separates at the anode, two anodic limit currents are observed; the first corresponds with the removal of iodide and oxidation to iodine; the second with the removal of iodide and iodine and oxidation to hypoiodous acid. In alkaline iodine solution two cathodic limit currents are observed; the first corresponds with removal of hypoiodite and reduction to iodide, the second with removal of iodate and reduction to iodide. The special form of the current *E.M.F.* curve in this case indicates that iodate is primarily reduced to iodite. In alkaline iodine solution one anodic limit current is observed, corresponding with the removal of iodide and oxidation to hypoiodite.

The limit current of the hypoiodite reduction has been studied with the view of throwing light on the kinetics of the chemical change hypoiodite \rightarrow iodate. The bimolecular character of this change is confirmed, and it appears very probable that iodos acid is involved as an intermediate product. The reaction in question is accelerated by platinum.

J. C. P.

Anodic Oxide Formation and Passivity. ERICH MÜLLER and FRITZ SPITZER (*Zeit. anorg. Chem.*, 1906, 50, 321—354. Compare this vol., ii, 158; Coehn and Osaka, *Abstr.*, 1903, ii, 261).—A considerable part of the paper is devoted to the classification of different cases of anodic oxide formation on the basis of Nernst's theory of *E.M.F.* The first large group includes instances of oxide formation with simultaneous change of valency, the cases (*a*) where the metal of the anode itself is dissolved, and (*b*) where the metallic ions in the solution take up extra charges, being distinguished. The other main group comprises cases of oxide formation without change of valency, and includes (*a*) the formation of simple from complex ions by the oxidation of one of the components of the latter, (*b*) the formation of simple ions from complex anions containing oxygen by increasing the hydrogen ion concentration at the anode.

The deposition on the platinum anode of the oxides of copper, silver, cobalt, nickel, iron, and aluminium by electrolysis of solutions containing complex ions in which the respective metals are present is described. In the case of copper, the complex ammonium salt was employed, and, owing to oxidation of the ammonia, the metal was deposited as hydrated cupric oxide. It was observed, however, that the proportion of water in the hydrated oxide was much less than that required for the formation of the normal hydroxide, and as in another experiment the green precipitated hydroxide, suspended in sodium hydroxide, was deposited on the anode during electrolysis as a black oxide containing very little water, it is considered that the current exerts a dehydrating effect by endosmotic action.

Iron, cobalt, and nickel can be made passive in various ways, and it has been suggested that this behaviour, as shown by the fact that on anodic polarisation in alkalis oxygen is evolved by small currents, as in the case of platinum, is due to the formation of a surface film of

oxide. With the object of testing this theory, platinum anodes have been coated with the finely-divided metals and with the oxides as described above, and it was found that the potential at which oxygen is evolved is exactly the same for the metal as for the oxide and much lower than for platinum itself, so that the anodic behaviour of the metals seems to be determined by a coating of oxide. The authors regard these results as strongly supporting the view that the passivity of the three metals in question, at least for anodic polarisation in alkali, is due to the presence of a surface film of oxide. G. S.

Ferromanganese Anodes in Solutions of Sodium Hydroxide. GEORGE R. WHITE (*J. Physical Chem.*, 1906, 10, 502—513).—When a current is passed with a ferromanganese anode through a solution of sodium hydroxide at the ordinary temperature, sodium permanganate is produced directly at the anode, irrespective of the concentration of the alkali or strength of current; any reduction to manganate occurring at this temperature is caused by organic impurity present in the solution. At 95°, however, the solution of permanganate is reduced to manganate by the hydrogen at the cathode; this is proved by surrounding the platinum cathode with a porous cell containing permanganate solution, using the ferromanganese anode in the solution of alkali hydroxide. An alkaline solution of permanganate does not undergo change at 95°; oxygen is not evolved as has been sometimes stated.

The formation of permanganate from a ferromanganese anode takes place even with very minute currents; it cannot owe its origin to the action of manganese on the alkali, because such action gives rise with a low current density only to manganous hydroxide.

Manganous hydroxide in presence of alkali can be oxidised electrolytically to manganese dioxide, but not to permanganate.

W. A. D.

Electrical Phenomena accompanying the Decomposition of Ammonium. I and II. ALFRED COEHN (*Chem. Centr.*, 1906, ii, 409—410; from *Nachr. K. Ges. Wiss. Göttingen*, 1906, 100—105, 106—109).—The assumption that the decomposition of metallic ammonium into non-metallic ammonia and hydrogen would be accompanied by radioactive phenomena was verified by presenting decomposing ammonium amalgam to an electroscope, when it was found that a visible deflection was produced with only 0.00004 gram of ammonium. The experiments were repeated with variations in the sensitiveness of the electrometer. The ammonium was shown to set free positive particles in decomposing. This evolution of positive particles is increased by giving the amalgam a positive charge, but is diminished by a negative charge. P. H.

The Electrocapillary Function. III. LÉON G. GOUY (*Ann. Chim. Phys.*, 1906, [viii], 9, 75—139).—A *résumé* of work already published (compare *Abstr.*, 1901, ii, 435, 592; 1902, ii, 194, 487; *Compt. rend.*, 1903, 136, 653). M. A. W.

Determination of Melting Points by Optical Methods. CORNELIO DOELTER (*Zeit. Elektrochem.*, 1906, 12, 617—621).—Many silicates fuse so slowly that their melting points are not marked by any retardation of the rise of temperature. In such cases the powdered substance is placed on a small plate of quartz heated in an electric resistance furnace and the powder observed by a microscope while the temperature is slowly raised. The beginning of fusion is marked by a rounding of the sharp edges, the angular particles finally being changed into vitreous drops. The powder may also be photographed at different temperatures. There is usually a considerable interval of temperature between the beginning and the end of the fusion. The following natural minerals were examined: albite, $\text{NaAlSi}_3\text{O}_8$, 1130° to 1215° ; oligoclase, $2\text{NaAlSi}_3\text{O}_8, \text{CaAl}_2\text{Si}_2\text{O}_8$, 1160° to 1240° ; labradorite, $3\text{NaAlSi}_3\text{O}_8, 4\text{CaAl}_2\text{Si}_2\text{O}_8$, 1185° to 1275° ; anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$, 1255° to 1340° . An artificial labradorite, $2\text{CaAlSi}_2\text{O}_8, \text{NaAl}_2\text{Si}_3\text{O}_8$, melted between 1190° and 1240° , and artificial anorthite, $\text{CaAlSi}_2\text{O}_8$, between 1275° and 1345° to 1350° . T. E.

Temperature of Non-luminous Flames Coloured by Metallic Salts. F. KURLBAUM and GÜNTHER SCHULZE (*Chem. Centr.*, 1906, ii, 486; from *Ber. Deut. physikal. Ges.*, 1906, 4, 239—247).—The author has measured the temperatures of various non-luminous flames on introducing metallic salts into them, and has obtained the following results: spirit flame, 1409° (Na_2CO_3)— 1476° (TiCl); Bunsen flame, 1660° (Na_2CO_3)— 1812° (RbCl); hydrogen flame, 1844° (LiCl)— 1954° (KCl). The temperature is increased by the introduction of a second salt, the increase being greater in proportion to the difference in wavelengths. The salts which relatively produce the greatest increase of temperature are those which are most highly ionised. P. H.

New Method for the Standardisation of Thermometers below 0° . THEODORE W. RICHARDS and FREDERICK G. JACKSON (*Zeit. physikal. Chem.*, 1906, 56, 362—365. Compare Richards, Abstr., 1903, ii, 354).—When a thermometer of known accuracy has been used to determine the freezing point of hydrochloric acid solutions of different strengths under standard conditions, then the depression-concentration curve obtained may serve as a means of standardising any other thermometer below 0° . The freezing point of a hydrochloric acid solution is determined with this second thermometer under the same standard conditions, and the acid solution is analysed. From the normal curve already obtained, the true freezing point of the solution may be read off, and the correction to be applied to the thermometer is thus ascertained. The following table gives the relationship found by the author between the strength of the hydrochloric acid solutions and the freezing point depression:

Depression of the freezing point.	Strength of solution.	Depression of the freezing point.	Strength of solution.
0.5°	0.139 normal	2.5°	0.663 normal
1.0	0.277 „	3.0	0.773 „
1.5	0.409 „	3.5	0.886 „
2.0	0.538 „	4.0	0.997 „

J. C. P.

Transition Temperature of Sodium Bromide. A New Fixed Point in Thermometry. THEODORE W. RICHARDS and ROGER C. WELLS (*Zeit. physikal. Chem.*, 1906, **56**, 348—361. Compare Richards and Churchill, *Abstr.*, 1898, ii, 555; 1899, ii, 354).—For the purposes of this research it was found impossible to purify sodium bromide satisfactorily by mere recrystallisation, and recourse was had to the preparation of hydrobromic acid from carefully purified bromine and subsequent neutralisation with pure sodium carbonate. The salt so obtained gave on analysis a weight of silver bromide which involves 23.008 as the atomic weight of sodium, if 107.93 and 79.955 are assumed as the atomic weights of silver and bromine respectively.

The transition temperature of the purest sodium bromide was determined with the usual precautions, and found to be 50.674° on the hydrogen scale. This transition point is very suitable for the standardisation of thermometers, although perhaps less accessible than the transition temperature of sodium sulphate, on account of the greater difficulty of procuring really pure sodium bromide. J. C. P.

Apparatus for Lecture Demonstration in Physical Chemistry. IWAN SCHRÖDER (*Chem. Centr.*, 1906, ii, 391; from *Zeit. chem. Apparatenkunde*, 1906, **1**, 427—430).—A thermoscope for demonstrating the thermal effects of solution, and a differential gas thermometer for showing the abnormal expansion of dissociating gases. P. H.

Calculation of Chemical Equilibria from Thermal Measurements. WALTHER NERNST (*Chem. Centr.*, 1906, ii, 397—400; from *Nachr. K. Ges. Wiss. Göttingen*, 1906, **1**—40).—A mathematical investigation of the relations between heat and chemical affinity. P. H.

A Thermochemical Relationship enunciated by Julius Thomson. EMIL BOSE (*Chem. Centr.*, 1906, ii, 595; from *Physikal. Zeit.*, **7**, 503—505).—Measurements of the heat change on mixing water with the various fatty alcohols show that this is not equal to zero at the boiling points of the alcohol-water mixtures, as has been stated to be the case by J. Thomson. The relationship holds approximately in the case of ethyl alcohol, but there are considerable deviations with methyl and propyl alcohols. H. M. D.

Comparisons between the Alkali and Alkaline Earth Oxides. ROBERT DE FORCRAND (*Ann. Chim. Phys.*, 1906, [viii], **9**, 139—144).—Certain thermo-chemical values of the alkaline and alkaline earth metals are tabulated in the original (compare this vol., ii, 445), and curves are also given in which these values as ordinates are plotted against the equivalents of the metals as abscissæ. In respect of all the thermo-chemical properties examined, lithium behaves as if it were an alkaline earth metal. M. A. W.

Studies in Vapour Composition. IV. HECTOR R. CARVETH and J. P. MAGNUSSON (*J. Physical Chem.*, 1906, **10**, 445—454).—The development is traced of the various forms of apparatus used in the

determination of molecular weight by the ebullioscopic method; the principal features of the more recent forms, involving vapour heating, are discussed, and a modified form is described for which the advantages claimed are: (1) that it is compact and easily manipulated; (2) that parts liable to break are easily replaceable. The special features of the new form are a reflux condenser provided with a mercury trap and a separate boiling vessel.

W. A. D.

Surface Tension of Aqueous Solutions. GÉZA ZEMPLÉN (*Ann. Physik*, 1906, [iv], 20, 783—797).—It was shown by Ramsay and Shields that the temperature-coefficient of the molecular surface energy of liquids is constant, the value being about 2.1. In the case of water, the value of the constant indicates association. The author has investigated the value in the case of aqueous solutions, taking as the molecular weight the value $(\mu_1 + c\mu_2)/\{1 + c(1 + d)\}$, where μ_1 is the molecular weight of water at the same temperature as determined from the surface tension, μ_2 the molecular weight of the solute, c the ratio of the concentrations of solute and water, and d the degree of dissociation. Experiments were made with solutions of silver nitrate, carbamide, and sodium chloride at various concentrations and temperatures, and the value of the constant is found to vary only between 2.05 and 2.31 throughout the whole range, indicating that the water has the same degree of association in its solutions as when pure. The constancy was better when the dissociation was allowed for than when it was neglected.

L. M. J.

Coefficient of Internal Friction of Mixtures of Argon and Helium. PAUL TÄNZLER (*Chem. Centr.*, 1906, ii, 487; from *Ber. Deut. physikal. Ges.*, 1906, 4, 222—235).—The measurements were made with the object of testing the formulæ proposed by Puluji, Sutherland, and Thiesen. Sutherland's formula for the connection between temperature and internal friction is trustworthy, whereas Puluji's formula is only approximately correct; Thiesen's theory was also confirmed. The following numerical values were obtained for the coefficients of internal friction at three temperatures. For argon, $\eta = 2200 \times 10^{-7}$ at 12° , 2746×10^{-7} at 99.6° , and 3231×10^{-7} at 183° ; and for helium, $\eta = 1969 \times 10^{-7}$ at 15.3° , 2348×10^{-7} at 99.6° , and 2699×10^{-7} at 184.6° . The addition of helium raises the coefficient for argon.

P. H.

Friction of Gaseous Mixtures. MAX THIESEN (*Chem. Centr.*, 1906, ii, 487; from *Ber. Deut. physikal. Ges.*, 1906, 4, 236—238).—It is pointed out that by means of the author's theory it is possible to calculate the coefficient of friction of any mixture of two gases for any temperature with the aid of eight, or possibly even fewer, constants.

P. H.

Dissociation of Water Vapour. I. H. VON WARTENBERG (*Zeit. physikal. Chem.*, 1906, 56, 513—533).—In measuring the dissociation of water vapour at high temperatures, two methods were used. In the first method, water vapour, either pure or mixed with small quantities

of electrolytic gas, was passed through a strongly heated vessel and the issuing gas was analysed. From the results of this analysis and the rate of passage of the water vapour, the equilibrium prevailing in the heated vessel could be ascertained. The vessel in question was constructed finally of porcelain, after silver, platinum, and quartz had been found unsuitable. Experiments of a preliminary nature were made by this method, and the percentage dissociation about 1130° was found to be nearly 0.007. These preliminary results indicate that the combination of hydrogen and oxygen about 1100° is a termolecular reaction, and experiments of a similar kind lead to the same conclusion in regard to the combination of carbon monoxide and oxygen at 1200 — 1300° .

The second method was essentially that used by Löwenstein (this vol., ii, 272), the temperature in the oven being determined by an optical method. The tube connected with the manometer (see *loc. cit.*) was constructed of iridium instead of platinum, and this allowed experiments to be carried out at higher temperatures, with the following results: 1882° , 1.18 per cent. dissociation; 1984° , 1.77 per cent. dissociation.

J. C. P.

Dissociation of Water Vapour. II. WALTHER NERNST and H. VON WARTENBERG (*Zeit. physikal. Chem.*, 1906, 56, 534—547. Compare preceding abstract).—In these more accurate experiments the authors passed a current of water vapour mixed with small quantities of electrolytic gas through a porcelain vessel shaped like a pipette. Of the two tubes attached to the bulb of this vessel, one was 0.5 mm. in diameter, the other was 6 mm. in diameter. Through the former the vapour from the vessel passed into a eudiometer tube filled with mercury; through the latter, a thermocouple was inserted into the bulb. The vessel was surrounded by a platinum tube, raised electrically to a high temperature, and this tube in its turn was embedded in magnesia.

The following values were obtained for the percentage dissociation at the temperatures given: 1124° , 0.0078 per cent.; 1207° , 0.0189 per cent.; 1288° , about 0.034 per cent. The experimental values are reproduced very satisfactorily by the formula: $\log 2x^3/P(2 + 0.01x)(1 - 0.01x)^2 = 11.46 - 25030/T + 2.38 \log T/1000 - 1.38.10^{-4}(T - 1000) - 0.685.10^{-7}(T^2 - 1000^2)$, where x is the percentage dissociation, P is the pressure of the gas mixture, and T is absolute temperature.

The paper contains also a calculation of the *E.M.F.* of the hydrogen-oxygen gas cell; it is found that $\epsilon = 1.232 - 0.00085(t - 17)$, a value which is probably correct to within a few millivolts (compare Preuner, *Abstr.*, 1903, ii, 51).

J. C. P.

General Method of Calculation in Kinetics: The Method of Areas. A Method of Approximate Effective Averages. RALPH E. DE LURY (*J. Physical Chem.*, 1906, 10, 423—444).—The author considers the methods hitherto available for the integration of differential equations of the general type $dx/dt = K(A - x)^l(B - x)^m(C - x)^n$, and suggests a new and simplified method of treatment. The

equation is used in the form $x = K \int_0^x F(x).dt$, or, in the case of reverse or successive reactions, in the form $x = K_1 \cdot \int_0^x F_1(x).dt \pm K_2 \cdot \int_0^x F_2(x).dt$.

The function $F(x)$ is plotted against t , and the areas $\int_0^x F(x).dt$ are measured by means of a planimeter; the values of K are calculated from the values of x and the correctness of the assumed function $F(x)$ tested. Alternative approximate methods of treatment are also given, and a comparison is made of the results of the different methods by applying them to a number of cases in which measurements have been made.

W. A. D.

Law of Distribution in the Case in which One of the Phases possesses Mechanical Rigidity: Adsorption and Occlusion.

MORRIS W. TRAVERS (*Proc. Roy. Soc.*, 1906, **78**, A, 9—22).—The author has investigated the occlusion of hydrogen and carbon dioxide by carbon and determined the pressure of the gas and its concentration in the solid at various temperatures between 100° and -78° in the case of carbon dioxide, and at -190° in the case of hydrogen. The results show that the pressure concentration curves may be represented by the formula $\sqrt[n]{p/x} = \text{constant}$, the value of x increasing as the temperature falls. Thus, in the case of carbon dioxide, $n = 2$ at 100° , and $= 3$ at 0° . At -78° , fair approximation to $\sqrt[5]{p/x} = \text{const.}$ is obtained. For hydrogen, at -190° , the value of n is approximately 3. The curves are similar in form to those obtained by Hoitsema for the occlusion of hydrogen by palladium (*Abstr.*, 1895, ii, 388), his isothermal at 0° being almost identical with that for carbon dioxide and carbon at -78° . The author does not consider the suggestion of Hoitsema, that the hydrogen is dissociated into single atoms, to be probable. The results are also analogous with those obtained by Schmidt (*Abstr.*, 1895, ii, 39) for the partition coefficient between charcoal and various solutions. As the author's results indicate an increase in the value of n , with increasing complexity of the gas, the complete removal of dyes, &c., from solution by charcoal is not surprising.

L. M. J.

Influence of Strong Electrolytes on Partition Phenomena.

HARRY M. DAWSON (*Zeit. physikal. Chem.*, 1906, **56**, 605—611).—In connexion with recent papers by Levin (this vol., ii, 527) and others, the author points out that earlier work by himself and McCrae (*Trans.*, 1901, **79**, 493) bears on the same subject. From this earlier work, and from experiments made by the author on the partition of iodine between water (or salt solutions) and carbon disulphide, it appears that the order of the anions, arranged according to the increasing magnitude of their influence in diminishing the solubility of ammonia and iodine in water, is: iodide, bromide, nitrate, chloride, oxalate, sulphate. The order is the same for ammonia and iodine, and, on the whole, parallel to that deduced from experimental work with other substances.

J. C. P.

Limited Miscibility of Liquids. The System Diphenylamine and Carbon Dioxide. ERNST H. BÜCHNER (*Zeit. physikal. Chem.*, 1906, 56, 257—318).—The author discusses the nature of the equilibrium liquid-vapour for a system of two partially miscible liquids, and the manner in which this equilibrium is affected by alterations of pressure, temperature, and concentration. In regard to the influence of temperature, three cases are distinguished: (1) the miscibility increases with falling temperature; (2) the miscibility increases with rising temperature and the two liquid phases become identical; (3) the miscibility increases with rising temperature, and one of the liquid phases becomes identical with the vapour.

The author discusses further the character of the equilibrium to be expected when the system comprises also one of the components as a solid phase. An example of one type is found in the system diphenylamine + carbon dioxide, for which some of the equilibrium curves have been experimentally traced. In this case the miscibility diminishes as the temperature rises. J. C. P.

A Specially Simple Case of Intermediate Reactions. EMIL ABEL (*Zeit. physikal. Chem.*, 1906, 56, 558—564).—When a reaction is studied which may take place in n stages (for example, the hydrolysis of a compound containing n groups capable of hydrolysis) the constancy of the expression $1/t \cdot \log a/(a-x)$ would usually be regarded as proof that the reaction (hydrolysis) was completed directly in one stage. The author points out, however, that the foregoing expression would be constant also where the reaction (hydrolysis) takes place in stages, provided that the velocity coefficients of the intermediate reactions fulfilled the following condition: $k_n : k_{n-1} : \dots : k_1 = n : n-1 : \dots : 1$. J. C. P.

Hydrolysis of the Esters of Polyhydric Alcohols. EMIL ABEL (*Zeit. Elektrochem.*, 1906, 12, 681—682).—The fact that the hydrolysis of ethylene diacetate and of triacetin by potassium hydroxide in homogeneous solutions are both bimolecular reactions is most simply explained by supposing that the velocities of hydrolysis of ethylene diacetate and monoacetate are in the ratio 2 : 1, and that the velocities for the three glyceryl salts are in the ratio 3 : 2 : 1. This is explained readily by the view that molecular collision must precede reaction, because in the salts containing two or three acid radicles the chance of impact between one of them and a hydroxyl group is two or three times greater than it is in the case of a salt with one acid radicle. T. E.

Kinetics of the Splitting-off of the Acyl Groups of the Esters of Polyhydric Alcohols by Hydroxyl Ions in Aqueous Homogeneous Systems. ROBERT KREMANN (*Monatsh.*, 1906, 27, 607—626. Compare *Abstr.*, 1905, ii, 630; *Lewkowitsch, Abstr.*, 1900, ii, 323; *Balbiano, Abstr.*, 1902, ii, 450; 1903, i, 547; this vol., i, 186).—The constants for the rates of the hydrolysis of ethylene diacetate and of triacetin by aqueous sodium hydroxide at 0° and 19·8°, when calculated by means of the formula for bimolecular reactions, remain almost

unchanged to the completion of the hydrolysis, when there is a slight diminution of the velocity, whereas if calculated for termolecular or for quadrimolecular reactions the velocity constant increases steadily. The hydrolysis of the esters of polyhydric alcohols is therefore a bimolecular reaction; the steadiness of the constant when calculated for a reaction of the second order shows that the rate of hydrolysis of the different acetyl groups must vary only slightly, so that the whole reaction resembles the hydrolysis of an ester of a monohydric alcohol by means of the equivalent amount of an alkali hydroxide.

Ethyl acetate has the average velocity of hydrolysis constant $k = 1.03$, ethylene diacetate $k = 2.5$, and triacetin $k = 3.6$ at 0° ; the velocity of hydrolysis of the ester of a dihydric alcohol is more than twice, and that of the ester of a trihydric alcohol more than thrice, that of the ester of a monohydric alcohol.

From the rates of hydrolysis of ethylene diacetate in 0.1 and 0.5*N*, and of triacetin in 0.073 and 0.485*N* solutions, the order of the reactions as calculated by van't Hoff's formula,

$$n = \log(dc_1/dt_1 : dc_2/dt_2) / \log(c_1 : c_2),$$

is for glycol diacetate $n = 2.4$, and for triacetin $n = 2.2$, but, as calculated by Noyes' formula, $n = 1 + \ln(t_1 : t_2) / \ln(c_2 : c_1)$; ethylene diacetate has $n = 1.92$, and triacetin $n = 1.88$, whilst for a reaction of the second order the theoretical value is $n = 2.00$.

The temperature-coefficients, as calculated from the rate of hydrolysis of ethyl acetate, ethylene diacetate, and triacetin at 0° and 19.8° , are $k_t + 10/k_t = 2.14, 2.25$, and 2.05 respectively. G. Y.

Earlier Methods for the Estimation of Hydrolysis. ALEXANDER NAUMANN and ADOLF RÜCKER (*J. pr. Chem.*, 1906, [ii], 74, 209—217).—A *résumé* of the methods which have been described by various authors for the estimation of hydrolysis. G. Y.

Estimation of Hydrolysis by Distillation. ALEXANDER NAUMANN and WILHELM MÜLLER (*J. pr. Chem.*, 1906, [ii], 74, 218—221. Compare preceding abstract).—The hydrolysis of sodium phenoxide in aqueous solution is estimated by distilling 500 c.c. of a solution of known strength from a flask, the volume being maintained constant throughout the distillation by addition of water; the amount of phenol is determined in an aliquot part of the distillate by titration with a solution of potassium bromide and bromate. A convenient form of apparatus, in which the distillate is collected in a burette cooled if necessary by a water-jacket, is described and figured.

This process is applicable to the estimation of hydrolysis in all cases, for example, ammonium salts, where a product of the hydrolysis distils with the solvent. G. Y.

Method for Determining Velocities of Saponification. JAMES WALKER (*Proc. Roy. Soc.*, 1906, 78, A, 157—160).—The progress of a chemical action in which electrolytes are involved may sometimes be followed by measuring the electrical conductivity of the solution at definite intervals (compare Walker and Kay, *Trans.*, 1897, 71, 489) when there is a considerable difference in conductivity between the initial and

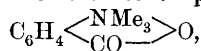
final stages of the action and the change in conductivity is proportional to the progress of the reaction. These conditions are fulfilled in the saponification of methyl acetate by sodium hydroxide; the divergence from the mean value of the constant for a bimolecular reaction is very small, so that the method is at least as accurate as the ordinary titration process, and much more convenient.

Details of the measurements and a simplified method for calculating the constant are given in the paper. G. S.

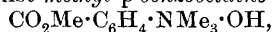
Cause of the Catalytic Effect of Hydrogen and Hydroxyl Ions on Hydrolytic Reactions. PAUL ROHLAND (*Zeit. physikal. Chem.*, 1906, **56**, 319—320. Compare Abstr., 1903, ii, 16).—It is supposed that the cause of catalytic acceleration in these reactions is the formation of undissociated water, which is specially reactive because it is *in statu nascendi*. This water is produced from the hydroxyl ion of water and the hydrogen ion of the acid, or from the hydrogen ion of water and the hydroxyl ion of the base. J. C. P.

Affinity Constants of Amphoteric Electrolytes. I. Methyl Derivatives of *p*-Aminobenzoic Acid and of Glycine. JOHN JOHNSTON (*Proc. Roy. Soc.*, 1906, **78**, A, 82—102. Compare Winkelblech, Abstr., 1901, ii, 370; Walker, Abstr., 1904, ii, 309; 1905, ii, 138).—The effect of successive introductions of a methyl group on the acid and basic strength of the two amino-acids at 25° has been investigated. The dissociation constant as base, k_b , was determined by the catalysis of methyl acetate; in the few cases in which this method was inapplicable, the solubility method of Löwenherz and the distribution method of Farmer and Warth (*Trans.*, 1904, **85**, 1713) were employed. The acidic constant, k_a , was determined either by electrical conductivity measurements (compare Walker, *loc. cit.*) or by the catalytic action of the sodium salt on methyl acetate, as employed by Shields (Abstr., 1893, ii, 448). It was found that the mono- and di-methyl derivatives of *p*-aminobenzoic acid can be prepared very satisfactorily by the action of methyl sulphate on the acid; under proper conditions the yields are almost quantitative.

The value of k_b for *p*-aminobenzoic acid, according to Winkelblech (*loc. cit.*), is 2.54×10^{-12} , and the majority of the methyl derivatives and esters prepared by the author show basic constants which do not differ greatly from that of the acid itself. *p*-Benzobetaine,



has k_b 32.3×10^{-12} , whilst *methyl p*-benzobetaine hydroxide,



is a strong base, since its hydriodide is not appreciably hydrolysed in aqueous solution. The values of k_a for mono- and di-methyl-*p*-aminobenzoic acid are 0.92×10^{-5} and 0.94×10^{-5} respectively, the acid itself having the value 1.21×10^{-5} . *p*-Benzobetaine, on the other hand, is a very weak acid, k_a being approximately 1×10^{-14} .

The methyl derivatives of glycine containing the carboxyl group, as well as trimethyl glycine (betaine) are rather weaker bases than that substance itself, whilst the methyl ester, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$, and ethyl

betaine hydroxide, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{NMe}_3\cdot\text{OH}$, are considerably stronger. Dimethyl glycine has $k_a 1.4 \times 10^{-10}$. The theoretical bearing of these results is discussed in the paper by Walker (see next pages). G. S.

Affinity Constants of Amphoteric Electrolytes. II. Methyl Derivatives of *o*- and *m*-Aminobenzoic Acids. ALEXANDER C. CUMMING (*Proc. Roy. Soc.*, 1906, **78**, A, 103—139. Compare preceding abstract).—The effect of successive introductions of a methyl group on the strength of *o*- and *m*-aminobenzoic acids, both as bases and acids, has been investigated. The determinations of the basic and acidic constants were made by the methods enumerated in the preceding abstract; in addition, the hydrogen ion concentration was determined in one or two cases by the ethyl diazoacetate catalysis method of Bredig and Fraenkel (*Abstr.*, 1905, ii, 692). The experiments were carried out at 25°. For the purpose of these measurements, several new substances have been prepared and examined.

Methyl m-aminobenzoate hydrochloride, $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{HCl}$, forms crystals melting and decomposing at 201—202°.

m-Methylaminobenzoic acid hydriodide, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NHMe}\cdot\text{HI}$, prepared by heating *m*-aminobenzoic acid and methyl iodide for three hours at 100° in a sealed tube, occurs in crystals melting and decomposing at 215°. The acid itself forms small, colourless crystals melting at 147°. An attempt was made to prepare this acid by interaction of molecular quantities of sodium *m*-aminobenzoate and methyl sulphate, but an orange-coloured substance was obtained, which proved to be a mixture of the mono- and di-methyl acids along with a trace of some coloured impurity. These acids could be separated by conversion into the hydrochlorides of the respective methyl esters and recrystallisation from cold alcohol. *Methyl m-methylaminobenzoate hydrochloride* forms crystals which melt and decompose at 75—78° and lose hydrogen chloride on exposure to air. The *ester*, obtained from the hydrochloride by treatment with water, forms crystals melting at 72°.

Methyl m-dimethylaminobenzoate hydrochloride,
 $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot\text{HCl}$,
 forms colourless crystals and melts at 175—177°.

m-Benzobetaine, $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix} \text{NMe}_3 \\ \text{CO} \end{smallmatrix}\right\rangle\text{O}$, was obtained by a modification of the method employed by Michael and Wing (*Abstr.*, 1886, 148) for the preparation of the *para*-compound. The hydriodide melts at 180°, the hydrochloride at 192°.

By the action of methyl sulphate on anthranilic acid, methyl-anthranilic acid, and not its methyl ester, is obtained (compare Willstätter and Kahn, *Abstr.*, 1904, i, 235). Ethyl methylanthranilate, $\text{NHMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$, is a colourless oil with an odour of jasmine, and solidifies below 18—20°.

Anthranilic acid has $k_b 1.3 \times 10^{-12}$; the constant for the methyl and ethyl esters is slightly larger, whilst the mono- and di-methyl derivatives of the acid have the respective values 0.94×10^{-12} and 0.28×10^{-12} . When, on the other hand, both the acidic and basic groups undergo methylation, the basic character is considerably enhanced. *o*-Benzobetaine has $k_b 0.28 \times 10^{-12}$, whilst the unstable

ethyl *o*-benzobetaine hydroxide is as strong a base as sodium hydroxide. The value of k_a for anthranilic acid is 1.04×10^{-5} , and the acidic character diminishes on successive replacement of the hydrogen atoms in the NH_2 group.

The basic constant for *m*-aminobenzoic acid is 13.3×10^{-12} . Its basic character is not seriously affected by successive replacement of the hydrogen atoms of the NH_2 group, but is increased by esterification, and still more when all the hydrogen atoms are replaced by methyl. The basic constant for *m*-benzobetaine is 34×10^{-12} , whilst methyl *m*-benzobetaine hydroxide is of the same order of strength as sodium hydroxide. The acidic constant for *m*-aminobenzoic acid is 1.63×10^{-5} ; for the mono- and di-methyl derivatives, 0.8×10^{-5} . *m*-Benzobetaine, like the corresponding *para*-compound, is an exceedingly weak acid.

The dilution law for simple (weak) bases is applicable to the hydrochloride of anthranilic acid.

The theoretical bearing of the above results is discussed in the paper by Walker (see below). G. S.

Affinity Constants of Amphoteric Electrolytes. III. Methylated Amino-acids. JAMES WALKER (*Proc. Roy. Soc.*, 1906, 78, 4, 140—149. Compare Abstr., 1904, ii, 309; 1905, ii, 138; Wegscheider, Abstr., 1895, ii, 310; 1902, i, 617; ii, 494; and two preceding abstracts).—The basic constant k_b of amino-bases and their alkyl derivatives is a function of the hydration as well as of the ionisation; both of which factors may be affected by substitution, whilst the acidic constant depends almost exclusively on the ionisation. Since the acidic constants of benzoic acid and phenylacetic acid are nearly equal, the basic constants of benzylamine and aniline might be expected to be approximately equal, and the fact that the latter is by far the weaker base is to be ascribed to difference of hydration. Similar reasoning applies to ammonia and the amines.

In amphoteric electrolytes there is the possibility of dehydration of the basic group and of ring-formation; the latter factor tends to diminish both acidic and basic constants. The small acidic constants of glycine and its derivatives point to extensive ring-formation due to the proximity of the acidic and basic groups.

When the mutual influence of the acidic and basic groups is slight, as in *p*-aminobenzoic acid, the esterification of the acid does not seriously affect the value of the basic constant, as shown by a comparison of the basic constants of the acid in question and its mono- and di-methyl derivatives with those of the corresponding esters. In the *ortho*-series, stereochemical influence is greater than in the *para*-series, but, although the basic constants of the mono- and di-methyl derivatives are much less than those of their esters, the value of k_b for the ester of anthranilic acid is only slightly greater than that of the acid itself, and therefore the great differences in the case of the methyl derivatives are probably to be referred to differences of hydration. The glycine esters have greater basic constants than the corresponding acids, as is to be expected from the magnitude of the stereochemical influence in these compounds. G. S.

Researches on Catalytic Racemisation. CHR. WINTHER (*Zeit. physikal. Chem.*, 1906, 56, 465—511).—The author has studied the rate at which active mandelic acid is racemised by heating with sodium or potassium hydroxide at 100° (compare Hollemann, *Abstr.*, 1899, ii, 282). The course of the racemisation is that of a reaction of the first order, and the values obtained for the velocity coefficient are nearly the same whether sodium or potassium hydroxide is used. The mandelic acid concentration exerts a relatively small influence on the velocity coefficient, but as the alkali concentration is increased the velocity coefficient increases rapidly, at a greater rate, in fact, than the alkali concentration. Some experiments were carried out at 87.3°, and it was found that a rise of 12.4° caused an increase in the velocity coefficient in the ratio 1:3.3.

The racemisation of *d*-tartaric acid under the influence of sodium or potassium hydroxide has also been studied (compare Meissner, *Abstr.*, 1897, i, 460; Hollemann, *Abstr.*, 1898, i, 515; Boeseken, *ibid.*, 561). For the purposes of this study a method was required for the analysis of mixtures of *d*-tartaric acid, racemic acid, and *i*-tartaric acid. The following procedure, a modification of ter Braake's method, was adopted. After racemisation of the active acid with sodium hydroxide, the liquid was neutralised exactly with nitric acid, and after being made up to a definite bulk was examined polarimetrically for the amount of active acid left unchanged. Then to a definite portion of the solution, slightly more than the calculated quantity of lead nitrate was added, along with acetic acid. The lead salts of *d*-tartaric and racemic acids are rapidly and completely precipitated, but for the complete precipitation of the lead salt of the inactive acid the solution must be stirred occasionally and allowed to remain overnight. The mixed lead salts are then decomposed by warming with a slight excess of 6*N* H₂SO₄ for a quarter of an hour on the water-bath. Of the filtrate from the lead sulphate one-half is carefully neutralised with dry potassium carbonate (phenolphthalein as indicator), and the other half is then added. The acid potassium salts of *d*-tartaric and racemic acids are completely precipitated by next day, and may then be filtered off, dissolved, titrated, and examined polarimetrically. Hence the amount of racemic acid is ascertained. The *i*-tartaric acid may be weighed as calcium salt or may be calculated by difference. In the cases where potassium hydroxide had been used as catalytic agent in the racemisation, a simpler analytical process could be employed, and it was then found that the amount of racemic acid found by the previous method must be corrected by a certain factor, the value of which is deduced from the author's experiments.

The course of the racemisation of *d*-tartaric acid with sodium hydroxide is that of a unimolecular reaction. The effect of altering the concentrations of tartaric acid and soda is generally similar to that observed in the case of mandelic acid. Similar remarks apply to the racemisation with potassium hydroxide. This substance, however, is less actively catalytic than sodium hydroxide in promoting racemisation, but as the excess of base over tartaric acid is increased the difference between the two hydroxides tends to diminish.

The author describes an improved method for the preparation of *i*-tartaric acid.
J. C. P.

Hydrates in Aqueous Solutions. WILHELM BILTZ (*Zeit. physikal. Chem.*, 1906, **56**, 463—464. Compare Abstr., 1904, ii, 710).—A further criticism of Jones' work (see Jones and Bassett, Abstr., 1905, ii, 687; and earlier abstracts). The author holds that Jones' theory is not original, and that his method of calculating the extent of hydration in solution is of doubtful value.
J. C. P.

Conductivity and Viscosity of Solutions of Certain Salts in Water, Methyl Alcohol, Ethyl Alcohol, Acetone, and Binary Mixtures of these Solvents. V. HARRY C. JONES and LEROY MCMASTER (*Amer. Chem. J.*, 1906, **36**, 325—409. Compare Abstr., 1903, ii, 55; 1905, ii, 73; 1906, ii, 66; and *Zeit. physikal. Chem.*, 1906, **56**, 129).—Determinations have been made at 0° and 25° of the electrical conductivity and the viscosity of solutions of lithium bromide and cobalt chloride in water, methyl alcohol, ethyl alcohol, acetone, and seventeen binary mixtures of these solvents. The results are tabulated and plotted as curves.

The conductivities of the solutions in mixtures of either of the alcohols or acetone with water exhibit a minimum which is more marked at 0° than at 25°, and is shown to be connected with the minimum in fluidity observed in these mixtures. The conductivity curves of lithium bromide in mixtures of methyl and ethyl alcohols are nearly straight lines, but in the case of cobalt chloride there is a slight sagging of the curves, which shows that the values obtained are rather less than would be expected from the law of averages.

The fluidity curves of solutions of lithium bromide in the alcohols, acetone, and in mixtures of these solvents are straight lines, indicating that mixtures of acetone and the alcohols do not form more complex aggregates than the pure solvents.

Both lithium bromide and cobalt chloride give a pronounced maximum in conductivity in mixtures of acetone with methyl or ethyl alcohol, which is regarded as being mainly due to a diminution in the size of the atmospheres about the ions. The change in the size of the ionic spheres is also considered to be a factor in the production of the minimum conductivity.

The temperature-coefficients of conductivity and fluidity are of the same order of magnitude. All the solutions of lithium bromide show with rise of temperature a large increase of conductivity due to increased fluidity, and the temperature-coefficients are therefore positive in all cases. Cobalt chloride, however, in some of the acetone mixtures at the ordinary temperature gives negative temperature-coefficients which are regarded as due not only to the effect of the diminishing dissociation in more than overcoming the increasing velocity of the ions, but also to the fact that the compounds formed by union of the solvent and solute may be more stable at higher temperatures. A dilution has been found for lithium bromide and cobalt chloride in a given mixture of solvents at which the temperature-

coefficient of conductivity is practically zero, and it is shown that the temperature-coefficients generally increase with the dilution both in aqueous and non-aqueous solutions. E. G.

Absorption of Gases by Charcoal. WILHELM VAUBEL (*J. pr. Chem.*, 1906, [ii], 74, 232—236).—"Gravito-affinity," that part of chemical affinity which is dependent on the mass or weight of the atoms or molecules in question, is directly proportional to the mass, as is shown by the close correspondence of the heats of dissociation and reaction determined with those calculated by multiplying the mol.-weight by the gravito-affinity factor, 1.12.

Assuming that the absorption of gases by charcoal is dependent on the gravito-affinity alone, the heat of absorption found when one gram-mol. of a gas is absorbed, multiplied by 1.12, must be equal to the gram-mol.-weight of the molecular compound of carbon and the gas absorbed. The results quoted show that 2 mols. of carbon dioxide or nitrous oxide, but only 1 mol. of sulphur dioxide, ammonia, chloroform, or hydrogen chloride, combine with four atoms of carbon. The number of atoms in the molecule of carbon must be four or some multiple of four, by which number the amount of any gas absorbed is limited.

G. Y.

Precipitation Membranes in Jellies and the Constitution of Gelatin Jelly. HEINRICH BECHHOLD and J. ZIEGLER (*Ann. Physik.*, 1906, [iv], 20, 900—918).—Two gelatin solutions containing respectively silver nitrate and sodium or barium chloride, lead nitrate and sodium chloride, magnesium sulphate and barium chloride, were separated by a layer of gelatin jelly, the strength of the gelatin being in all cases 10 per cent. By diffusion, a precipitate was formed in the central layer, and this precipitate was permeable to the salts producing it, and increased in thickness in the direction of the lower osmotic pressure. If the solutions on either side are of equal osmotic pressure, this diffusion, however, does not occur, the precipitate membrane appearing to be impermeable. Two gelatin solutions were next separated by a jelly containing, diffused through it, a precipitate of silver chloride or barium sulphate, and it was found that this layer was permeable, diffusion occurring in both directions. Experiments were also made with copper or zinc ferrocyanide membranes, which were found to be impermeable to the potassium ferrocyanide. The authors consider that the jelly acts as a network of gelatin with pores filled with water, through which alone the diffusion takes place. The rôle of the precipitate is merely the filling of these pores and the consequent prevention, partial or complete, of the diffusion. L. M. J.

Capacity of the Elements for entering into Chemical Combination. RICHARD ABEGG (*Zeit. anorg. Chem.*, 1906, 50, 309—314). Compare Abstr., 1904, ii, 475; Tammann, this vol., ii, 346).—In connection with Tammann's paper on this subject, the author recapitulates his views on the valency and polar nature of the elements, and shows that the two laws established by Tammann for the combining capacity of the elements among themselves are conveniently represented by his

theory, which also accounts satisfactorily for some of the deviations from the laws. G. S.

Relations between Structure and Odour in Organic Compounds. GERTRUD WOKER (*J. Physical Chem.*, 1906, 10, 455—473). —A classification of a large number of odoriferous substances according to their chemical structure. The following are the principal conclusions drawn. Saturated compounds rarely produce odour, and then only in the case of very volatile substances. The volatility is increased especially by loading a carbon atom with identical groups; substances in which all the hydrogen of at least one carbon has been replaced often have an odour like that of camphor, when at least two of the substituents are identical. In these circumstances it is indifferent whether the compound is unsaturated or saturated, but, in the latter case three of the substituent groups must be the same. With other conditions the same, the intensity of odour increases as the degree of saturation is diminished. Substances with a triple linking have usually a more marked odour than corresponding substances containing a double linking, and the presence of several double or triple linkings increases the odour. W. A. D.

Shortened Manometer with Reproducible Vacuum. LEO UBBELOHDE (*Chem. Zeit.*, 1906, 30, 966. Compare this vol., ii, 432). —A vacuum gauge which can be easily cleaned and can be employed for measuring high or low vacua. For diagrams and details the original should be consulted. P. H.

Inorganic Chemistry.

Action of Fluorine on Chlorine ; a New Method of Forming Hypochlorous Acid. PAUL LEBEAU (*Compt. rend.*, 1906, 143, 425—427).—Moissan has shown that fluorine and chlorine do not combine at the ordinary temperature or on warming ; the author has examined the action of fluorine on chlorine at low temperatures, and finds that fluorine dissolves in liquid chlorine at -80° , but no definite compound is formed, for on fractionally distilling the solution, the gases evolved at the beginning, the middle, and the end of these operations contained respectively 97.32, 91.40, and 0.63 per cent. of fluorine ; further, on cooling the solution, either slowly or rapidly, it solidifies suddenly with a tumultuous evolution of gas ; the solid consists of pure chlorine and the gas of fluorine.

When fluorine is passed into chlorine water, hypochlorous acid is formed according to the equation $2\text{H}_2\text{O} + \text{Cl}_2 + \text{F}_2 = 2\text{HF} + 2\text{ClOH}$.

M. A. W.

Atomic Weight of Bromine. GREGORY P. BAXTER (*Zeit. anorg. Chem.*, 1906, **50**, 389—402. Compare Scott, *Trans.*, 1901, **79**, 147).—From eighteen concordant determinations of the ratio $\text{Ag}:\text{AgBr}$ made by Richards and his co-workers in recent years, the value 79.956 ($\text{Ag}=107.930$) is obtained for the atomic weight of bromine, in excellent agreement with Stas's value from the synthesis of the bromide, 79.954. As, however, increased experience in the purification of the materials has been gained since some of these determinations were made, it has been considered desirable to make a fresh series of experiments.

The bromine was reduced to hydrobromic acid and treated repeatedly with potassium permanganate or free bromine to free it completely from iodide; after reconversion into bromine, it was distilled several times from bromide solution to remove traces of chlorine. The silver, the greater part of which had already been used for atomic weight determinations, was obtained in crystalline form by electrolysis of its solution, and the crystals, in a boat of lime, were melted in a current of hydrogen to remove traces of oxygen.

Two series of experiments were made; in the first the ratio $\text{Ag}:\text{AgBr}$ was determined by dissolving a known weight of silver in nitric acid, precipitating with ammonium bromide, washing, drying, and fusing the precipitate. In the second series, a weighed amount of the bromide was changed to chloride by heating in a glass tube through which a slow current of chlorine was passed.

Eighteen very concordant determinations of the ratio $\text{Ag}:\text{AgBr}$ with five different samples of silver and bromine respectively gave for the atomic weight a mean value of 79.953. Thirteen determinations from the ratio $\text{AgBr}:\text{AgCl}$ gave a mean of 79.952 ($\text{Cl}=35.473$). The mean of the two series is taken as 79.953, in excellent agreement with Stas. Scott's result is somewhat lower. G. S.

Preparation of Ozone from Oxygen and Atmospheric Air by the Silent Discharge from Metallic Electrodes. III. EMIL WARBURG and G. LEITHÄUSER (*Ann. Physik*, [iv], 1906, **20**, 734—742. Compare *Abstr.*, 1905, ii, 516).—The authors have investigated further the best conditions for the preparation of ozone by the silent discharge from metallic electrodes, and have determined the yield of ozone per ampere hour and per kilowatt hour under various conditions. For small concentrations up to 4 grams of ozone per cubic metre, the discharge from a highly charged positive sphere is best; for higher concentrations up to 9 grams of ozone per cubic metre, the discharge from a negatively charged sphere is best. In the latter case, at the concentration of about 8—9 grams per cub. metre, a yield of about 30 grams of ozone per kilowatt hour is obtained. L. M. J.

Equilibrium Point in the Formation and Decomposition of Ozone by the Action of the Electrical Discharge from Points in Oxygen. P. CERMAK (*Chem. Centr.*, 1906, ii, 585; from *Ber. Deut. physikal. Ges.*, **4**, 268—276).—The equilibrium between ozone and oxygen is dependent on the temperature, pressure, and purity of the gas, and varies also with the shape of the electrode, its positive or

negative sign, and the intensity of the current. Rise of temperature or fall of pressure diminishes the proportion of ozone. The influence of impurities and of the distance between the electrodes is comparatively small, but the equilibrium varies with the thickness of the electrode. With a negatively-charged point, the proportion of ozone is much greater than when the point is positive. H. M. D.

Influence of Moisture and Temperature on the Ozonisation of Oxygen and Atmospheric Air. EMIL WARBURG and G. LEITHÄUSER (*Ann. Physik*, 1906, [iv], 20, 751—758).—A number of tables and curves are given for the formation of ozone against pressure of water-vapour. The results show that the formation of ozone both in oxygen and air is reduced by the presence of moisture, the reduction being greater in oxygen than in air. By rise of temperature to 80° at constant density, the ozonisation in oxygen is but little altered; in air it is perceptibly reduced. L. M. J.

Production of Ozone by Electrolysis of Alkali Fluorides. E. B. R. PRIDEAUX (*Trans. Faraday Soc.*, 1906, 2, 34—35).—Using a current density of 100 amperes per square decimetre in the electrolysis of aqueous hydrofluoric acid, the author obtained 0.23 per cent. of ozone. The electrolysis of potassium fluoride with a current density of 10 amperes per square decimetre gave a maximum yield of 0.65 per cent. of ozone in twenty minutes. P. H.

Oxidising Power of the Air on a Mixture of Potassium Iodide and Arsenite at Various Points on Mont Blanc. ROBERT LESPIEAU (*Bull. Soc. chim.*, 1906, [iii], 35, 616—619).—The author finds, from observations made during August and September in 1900 and 1901, that the quantity of ozone contained in the air above the glaciers of Mont Blanc is about 4.5 milligrams in 100 kilograms, the proportion being independent of the altitude. This result is based on the assumption that the oxidation of the solution of potassium iodide and arsenite used for the estimation is entirely due to ozone, and that in the gas-washing apparatus used, all the ozone is reduced. This result does not confirm de Thierry's statement (*Abstr.*, 1897, ii, 253), that the amount of ozone present in the air on Mont Blanc increases with the altitude. Descriptions of the solutions used, the apparatus employed, and the method of conducting the observations, as well as a tabular statement of results, are given in the original. T. A. H.

Oxides of Hydrogen Sulphide. EMIL FROMM and JOSÉ DE SEIXAS PALMA (*Ber.*, 1906, 39, 3317—3326. See this vol., i, 819).

Aldehyde Bisulphites and [the Constitution of] Hypo-sulphites. HANS BUCHERER and ARTHUR SCHWALBE (*Ber.*, 1906, 39, 2814—2823. Compare Bernthsen, *Abstr.*, 1905, ii, 240, and Bazlen, *Abstr.*, 1905, ii, 240).—The view of Bernthsen and Bazlen, that the hyposulphites are salts of a mixed anhydride, $\text{SONa} \cdot \text{O} \cdot \text{SO}_2\text{Na}$, of sulphurous and the hypothetical sulphonylic acid, is opposed in favour

of a symmetrical constitution and a direct junction between the two sulphur atoms of the hyposulphite, $\text{SO}_2\text{Na}\cdot\text{SO}_2\text{Na}$ or $\text{O} \begin{array}{c} \text{SO}_2\text{NaH} \\ | \\ \text{SO}_2\text{NaH} \end{array}$.

E. F. A.

Hybrid Elements. MAX LE BLANC (*Zeit. Elektrochem.*, 1905, 11, 813—818; 1906, 12, 649—654).—A thin coating of sulphur or selenium on a platinum cathode in potassium hydroxide solution goes into solution in the form of polysulphide or polyselenide ions. These elements do not, however, dissolve when used as cathodes. Tellurium, on the other hand, dissolves in normal potassium hydroxide solution both as cathode and as anode. At the cathode it yields a red solution of polytelluride. At the anode it dissolves with a valency of nearly four, in the form of Te^{+++} ions, the greater part of which react with hydroxyl ions, forming TeO_3^{--} ions.

Tellurium is insoluble in a normal solution of potassium hydroxide from which oxygen is excluded. In a 10*N*-solution, however, it dissolves at 100° to a red solution, from which it separates again on cooling or dilution. This points to the simultaneous presence of positive and negative tellurium ions. A red solution prepared by cathodic solution of tellurium, and containing only negative ions, is permanent. No tellurium dissolves when an alternating current is passed between tellurium electrodes in *N*-potassium hydroxide solution, but in 10*N*-solution dissolution takes place, the quantity dissolved increasing as the number of alternations per minute decreases. Red solutions are formed from which tellurium soon begins to separate.

The observations are most simply explained by supposing that tellurium dissolves at the cathode in the form of Te^- ions, and at the anode as Te^{+++} ions. Equilibrium exists in solution between these ions and free tellurium, $3\text{Te} \rightleftharpoons 2\text{Te}^- + \text{Te}^{+++}$. In very concentrated alkaline solutions, the equilibrium requires the presence of measurable quantities of the substances on the right-hand side of the equation, but in dilute solutions it is displaced almost entirely towards the left-hand side of the equation.

T. E.

Behaviour of Selenium towards Light and Temperature. III. ROBERT MARC (*Zeit. anorg. Chem.*, 1906, 50, 446—464. Compare Abstr., 1904, ii, 105; this vol., ii, 226).—As a result of further investigations, it is now found that the small conductivity with positive temperature-coefficient ascribed to the *A* variety of selenium (*loc. cit.*) was due to the presence of traces of the dioxide; this variety, prepared in an atmosphere of nitrogen or carbon dioxide, is practically a non-conductor. The conductivity of selenium containing a definite proportion of the dioxide has been investigated at different temperatures, and a formula representing the change of conductivity with temperature is suggested.

The equilibrium between the *A* and *B* forms at different temperatures, and the conductivity of the mixtures, has been further studied. It has been found that small amounts of silver (even 0.03 per cent.) very greatly facilitate the attainment of the equilibrium, and it has

thus been possible to obtain measurements of the conductivity of equilibrium mixtures at temperatures between 20° and 210° . The curve shows a maximum about 100° , and this is regarded as being due to the combined effect of the increase of conductivity of *B* with fall of temperature, and the simultaneous displacement of the equilibrium in the direction of the non-conductor *A*. The conductivity of mixtures in the absence of catalysts, and, therefore, far removed from the equilibrium point, has also been determined, and the results find a satisfactory interpretation on the above view.

The question of the sensitiveness of selenium to light is being further investigated on the basis of these results. G. S.

Some Physical Constants of Ammonia: a Study of the Effect of Change of Temperature and Pressure on an Easily Condensible Gas. EDGAR P. PERMAN and JOHN H. DAVIES (*Proc. Roy. Soc.*, 1906, **78**, *A*, 28—42).—The experiments were undertaken chiefly to determine the vapour density of ammonia, the result obtained for 0° in grams per litre at latitude 45° being 0.77085, agreeing well with the result 0.7708 obtained by Guye (*Abstr.*, 1905, *ii*, 506). From Lord Rayleigh's value for the compressibility, the molecular weight is hence calculated as 17.030 ($H=1.0076$), and the atomic weight of nitrogen therefore 14.007, a value in accord with recent results. The author found that no appreciable adsorption or condensation of ammonia occurs with dry glass vessels. The pressure coefficient between 0° and 98° at atmospheric pressure is 0.003802, and the coefficient of expansion 0.003847, the corresponding values between 0° and -20° being 0.004003 and 0.003914. The vapour pressure of pure ammonia at various temperatures was also determined by one of the authors, the results being -49.8° , 297.95 mm.; -41° , 530.95 mm.; -30° , 866.95 mm.; -20° , 1392.9 mm.; -15° , 1726.2 mm.; -10° , 2145.9 mm.; -5° , 2616.9 mm. By interpolation, the boiling point at 760 mm. is obtained as -33.5° . L. M. J.

Oxidation of Nitrogen by the Action of the Silent Discharge in Atmospheric Air. EMIL WARBURG and G. LEITHÄUSER (*Ann. Physik*, 1906, [iv], **20**, 743—750).—Simultaneously with the partial ozonisation of the atmospheric oxygen, some of the nitrogen is oxidised. The estimation of the oxides of nitrogen was facilitated by the fact that, in the presence of ozone, they are completely absorbed by a dilute solution of sodium hydroxide. It is found that for a silent discharge from a positive sphere in atmospheric air at the ordinary temperature, a quantity of nitrogen corresponding with 10 litres of nitric oxide is oxidised per ampere-hour, this amount being independent of the quantity of moisture in the air. The quantity of nitrogen oxidised at first increases with rising temperature and afterwards, like the ozone formation, decreases. A quantity of nitric peroxide corresponding with 1 per cent. of nitric oxide per 1500 c.c. prevents the formation of ozone. L. M. J.

Solubility of Nitric Oxide and of Air in Sulphuric Acid. OLIN F. TOWER (*Zeit. anorg. Chem.*, 1906, **50**, 382—388).—The measurements were made in an absorption tube over mercury. In

mixtures containing 50—80 per cent. of sulphuric acid, the solubility is practically constant, about 0.0115 c.c. per c.c. of liquid at 18° under atmospheric pressure; for 90 per cent. acid it is 0.0193. The gas has no definite solubility in 98 per cent. sulphuric acid, as mercury is slowly dissolved and the volume of the gas decreases. The acid used in the Lunge nitrometer should not be over 90 per cent., and in these circumstances the error due to the solubility of nitric oxide is negligible.

The coefficient of solubility of air in sulphuric acid at 18° is very small; for 98 per cent. acid it is 0.0173, and for 70 per cent. acid attains a minimum value of 0.0055. G. S.

Hypophosphoric Acid. NICOLÒ PARRAVANO and C. MARINI (*Atti R. Accad. Lincei*, [v], 15, ii, 203—211).—Measurements of the electrical conductivity at different concentrations of aqueous solutions of the sodium hypophosphates NaHPO_3 and Na_2PO_3 are given; from the variation of the conductivity on dilution, the conclusion is arrived at that the former salt really corresponds with the formula $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6$, the normal salt being $\text{Na}_4\text{P}_2\text{O}_6$, both salts undergoing decomposition in the more dilute solutions. [Compare, however, following abstract.]

Values are given for the conductivities of solutions containing molybdic acid and sodium hypophosphate in the molecular proportions $\text{Na}_4\text{P}_2\text{O}_6 : \text{MoO}_3 = 1 : 1$, $1 : 2$, $1 : 3$, and $1 : 4$. The molybdic acid appears to condense continuously with the hypophosphate in the more concentrated solutions, but in the more dilute solutions decomposition of the aggregates occurs. The same equilibrium is attained in the case of the proportion $\text{Na}_4\text{P}_2\text{O}_6 : \text{MoO}_3 = 1 : 2$, by starting with either sodium hypophosphate and molybdic acid, or sodium molybdate and hypophosphoric acid; in the latter case, the action $2\text{Na}_2\text{MoO}_4 + \text{H}_4\text{P}_2\text{O}_6 = \text{Na}_4\text{P}_2\text{O}_6 + 2\text{MoO}_3 + 2\text{H}_2\text{O}$ occurs. W. A. D.

The Molecular Weight of Hypophosphoric Acid. ARTHUR ROSENHEIM, WILHELM STADLER, and FELIX JACOBSON (*Ber.*, 1906, 39, 2837—2844; *Salzer, Abstr.*, 1886, 420; *Bansa, Abstr.*, 1894, ii, 279).—A modified method for the preparation of sodium hydrogen hypophosphate is described. Its aqueous solution is faintly alkaline to phenolphthalein, but neutral to methyl-orange. Electrical conductivity determinations have been made with the acid salt and with this salt and an equivalent of sodium hydroxide; the conclusions drawn are that the salt is an acid salt, but that in the presence of an equivalent of sodium hydroxide free hydroxyl ions are present. The following numbers for the equivalent conductivity of the salt:

<i>v</i>	16	32	64	128	256	512	1024
λ	40.8	44.0	47.2	50.1	53.0	56.0	60.8

agree best with the view that the salt has the simple formula NaHPO_3 and not the bimolecular formula. [Compare, however, preceding abstract].

The freezing-point curve for mixtures of phosphorous and phosphoric acids is of the normal form for a pair of compounds which form neither isomorphous mixtures nor chemical compounds. The hypo-acid is thus not formed by fusing a mixture of phosphorous and phosphoric acids.

Methyl hypophosphate has the simple formula Me_2PO_3 , and ethyl pyrophosphate the formula $\text{Et}_4\text{P}_2\text{O}_7$, as shown by ebullioscopic determinations in ethyl bromide, ethyl iodide, and chloroform.

Ethyl hypophosphate could not be prepared, the final product being the pyrophosphate. J. J. S.

Quantitative Vaporisation of Phosphoric Acid from its Salts. PAUL JANNASCH and E. HEIMANN (*Ber.*, 1906, 39, 2625—2628).—If a phosphate is mixed with sugar, and sulphuric acid then added so as in this manner to obtain an intimate mixture of the phosphate and charcoal, it is possible to distil off the phosphoric acid quantitatively in a stream of chlorine. Details are given of experiments carried out in this manner with ammonium hydrogen phosphate and ammonium magnesium phosphate respectively. A. McK.

An Allotropic Form of Arsenic. WILLIAM THOMSON (*Mem. Manchester Phil. Soc.*, 1906, 50, (12), 1—3. Compare Erdmann and von Unruh, *Abstr.*, 1903, ii, 73).—The yellow arsenic obtained by the rapid cooling of arsenic vapour in a vacuum or in an atmosphere of an inert gas blackens almost instantaneously under the influence of magnesium light. Its rate of transformation in the dark is increased by a rise of temperature. In liquid air, the yellow form remains unchanged for hours. H. M. D.

Preparation of Boron Sulphide from Ferroboron. J. HOFFMANN (*Zeit. angew. Chem.*, 1906, 19, 1362—1363).—Boron sulphide may be prepared by passing a current of dry hydrogen sulphide over powdered ferroboron heated at 300—400° in a long combustion tube, to the end of which is attached a U-tube cooled in ice. Close to the source of heat the boron sulphide which is formed condenses to a yellowish-white, glassy mass containing a small quantity of sulphur produced by the decomposition of the hydrogen sulphide, whereas farther away it condenses to a mass of white, glistening crystals; at the end of the tube it condenses in an amorphous form. Any fumes escaping with the hydrogen sulphide are condensed in the U-tube. The residue, after heating, is found to consist of iron, sulphur, and boron.

P. H.

Rate of Action of Oxygen, Carbon Dioxide, and Water Vapour on Carbon. PEDER FARUP (*Zeit. anorg. Chem.*, 1906, 50, 276—296).—For the measurements referred to in the title, the carbon, in the form of slender rods, was placed in a wide porcelain tube connected at one end with a narrow glass tube and at the other with a capillary exit tube; the porcelain tube was heated in an electric furnace, the respective gases passed through it at a definite rate, and afterwards collected and analysed. To facilitate comparison of the results, the measurements with the different gases were made under exactly corresponding conditions.

Carbon dioxide and water-vapour react with carbon at 850° with practically equal velocity, whilst oxygen attains the same rate at 450°. The temperature-coefficient of the latter reaction between 450° and

500° has been determined, and the reaction velocity between oxygen (at atmospheric pressure) and carbon at 850° calculated by extrapolation; it is 3×10^6 times as great as that of the other two gases under the same conditions. The dissociation of carbon dioxide and of water vapour has been determined quite recently by Nernst and Wartenburg (Abstr., 1905, ii, 629), and from their observations it is shown that the oxygen concentration in these two gases at 850° is about equal, and about $1/0.7 \times 10^6$ that of oxygen under the same conditions. From this it follows that the reaction-velocity in all three cases is approximately proportional to the oxygen concentration, and it seems plausible to assume that it is the rate of reaction between carbon and oxygen which is being measured in each case, the respective reactions, $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2$ and $2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$, being rapid in comparison. On this view the time reaction between carbon and oxygen is $2\text{C} + \text{O}_2 = 2\text{CO}$, the reaction $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ being much more rapid.

It has, however, been found very difficult to bring the results of some measurements on the rate of reaction between carbon dioxide and carbon at 1050° into agreement with this view. The reaction-velocity is approximately proportional to the square of the concentration of the carbon dioxide, and if the primary reaction is $2\text{CO}_2 = 2\text{CO} + \text{O}_2$ this can only be accounted for on certain rather improbable assumptions. So far, no satisfactory explanation of this discrepancy has been obtained. G. S.

Action of Selenium on Carbon Tetrabromide. A. VON BARTAL (*Chem. Zeit.*, 1906, 30, 810—812).—On distilling a mixture of 1 mol. of carbon tetrabromide with 2 mols. of amorphous red selenium, a small quantity of a reddish-yellow oil passes over between 160° and 190°; the fraction distilling about 190° sets to a red solid on cooling. The residue, after extraction alternately with carbon disulphide, phenol, alcohol, and ether, yields a greyish-black powder having the composition $\text{C}_9\text{Br}_2\text{Se}_4$; it decomposes at high temperatures and dissolves in concentrated sulphuric acid to a reddish-brown solution. Heated with very concentrated sodium hydroxide it gives a substance of the composition C_4Se ; this compound dissolves with difficulty in hot concentrated sulphuric acid to a light brown solution. Hydrochloric acid added to the sodium hydroxide solution precipitates the compound C_5Se_2 , a violet-brown powder which dissolves readily in hot concentrated sulphuric acid to a reddish-brown solution; on prolonged heating, the colour gradually becomes lighter. The phenol extract of the residue from the distillation, on boiling with aqueous alcohol, gives a brown, flocculent precipitate of the composition $\text{C}_{10}\text{BrSe}_5$; this substance, which is greyish-brown and amorphous, dissolves readily in hot concentrated sulphuric acid to a brown solution; it does not sublime or melt. On boiling with very concentrated sodium hydroxide, it is converted into the substance C_5Se_2 . The carbon disulphide used in the purification of the compound $\text{C}_{10}\text{BrSe}_5$ yields, on evaporation, a small quantity of crystals with a red, metallic lustre, which melt at 120° and have the composition $\text{C}_3\text{BrSe}_3 \cdot 3\text{H}_2\text{O}$. From the carbon disulphide used in extracting the original distillation residue are obtained a black liquid and a reddish-brown, shiny substance: the latter

consists chiefly of selenium, whilst the former, on oxidation, gives carbon oxybromide, and also yields an orange-coloured solid of the composition $C_3Br_2Se_2$, which darkens at 150° and melts at $210\text{--}212^\circ$; it dissolves fairly readily in carbon disulphide to a yellow solution which decomposes on warming.

The first fraction of the distillation boiling at $160\text{--}190^\circ$, which consists of 2 or 3 c.c. of a reddish-yellow oil, yields, on purification, transparent, brownish-red leaflets which melt at 154° ; this substance is slightly soluble in hot carbon disulphide, but readily soluble in concentrated sulphuric acid, and has the composition $C_2Br_2Se_4$.

Constitutional formulæ for the substances described are proposed.

P. H.

Oxidation by Burning Potassium. KARL A. HOFMANN and H. HIENDLMAIER (*Ber.*, 1906, **39**, 3184—3187).—Platinum, gold, copper, iron, nickel and cobalt are readily attacked by burning potassium, whereas silver is only slightly attacked.

When potassium is burned on a nickel trough, a mixture of yellowish-brown potassium tetroxide and long, black prisms is obtained. When water is added to this product, the potassium tetroxide is decomposed into oxygen and potassium hydroxide and a black, crystalline powder subsides, which, when washed and dried, consists of raven-black, metallic prisms of the compound, $Ni_2O_5H_4$; the latter oxidises organic substances readily. It is probably nickelous nickelite, $NiO_2 \cdot NiO \cdot 2H_2O$.

The black prisms obtained from the action of potassium on nickel, before the mass is treated with water, is probably *potassium nickelo-nickelite*, $NiO_2 \cdot NiO \cdot K_2O$.

Cobaltous cobaltite, $CoO \cdot 2CoO_2 \cdot 2H_2O$, prepared by the action of cobaltous oxide on fused potassium peroxide, crystallises in hexagonal, glistening plates. It is much more stable than the corresponding nickelous nickelite.

A. McK.

Solid Polyiodides of the Alkali Metals, their Stability and Conditions of Existence at 25° . RICHARD ABEGG and ANNA HAMBURGER (*Zeit. anorg. Chem.*, 1906, **50**, 403—438. Compare Johnson, this Journal, 1877, i, 249; Wells and Wheeler, *Abstr.*, 1893, 67, 68).—The method of investigation was as follows: according to the phase rule, two solid phases, in the present case iodine and an iodide or two iodides, are in equilibrium with a definite concentration of iodine, but if, by addition of the monoiodide sufficient iodine is withdrawn, the higher solid phase disappears, and there being now only one solid phase the concentration of iodine in the solution will be variable until reduced to such an extent that a still lower iodide makes its appearance, when it again becomes constant. Proceeding in this way, the lowest polyiodide is reached finally, which is in equilibrium with the monoiodide and a constant concentration of iodine. If, on the other hand, the iodine concentration is gradually increased, higher polyiodides are obtained until the limit of saturation for iodine is reached, when iodine and the highest attainable iodide are the solid phases. The composition of

the individual polyiodides is determined by analysis of the solid phases in contact with the variable concentrations of iodine.

The iodine was used in benzene solution, the substances being shaken together for long periods with occasional analysis of a small portion of the supernatant liquid; in the majority of cases, the equilibrium was reached from both sides. The compounds obtained, with the relative iodine concentrations with which the respective pairs are in equilibrium, are as follows (concentration of iodine in saturated benzene solution = 1): $KI_7 - KI = 0.611$; $NH_4I_3 - NH_4I = 0.053$; $RbI_3 - RbI = 0.0256$; $RbI_7 - RbI_3 = 0.63$; $RbI_9 - RbI_7 = 0.732$; $CsI_3 - CsI = 0.00331$; CsI_5 or $CsI_7 - CsI_3 = 0.155$; $CsI_9 - CsI_3 = 0.514$; $CsI_9 - CsI_5 = 0.94$ (calculated). The tri-iodides of potassium, sodium, and lithium could not be obtained, as their tensions at 25° are greater than that of iodine itself. The results are not quite conclusive as regards the higher iodides of caesium; the tri-iodide is in certain circumstances in equilibrium with CsI_9 , although there are indications of the existence of an intermediate compound, the composition of which has not been definitely determined.

The solubility of iodine in very concentrated solutions of potassium iodide, up to 5.5 normal, was determined. The ratio $KI:I_2$ for the latter solution is 1:3.10, and it has a sp. gr. of 2.75. A solution of potassium iodide, saturated at 25° is 6.15*N* and contains 1002 grams of the salt per litre of solution. It follows that the solubility of potassium iodide is practically unaffected by the presence of these large proportions of iodine. The ratio of iodide to iodine is far below that required by the formula KI_7 , so that the latter is partially split up into its components in water at 25° .

The freezing-point curve of mixtures of iodine and potassium iodide, up to rather more than 50 per cent. of the latter, has also been determined. It falls from the freezing-point of iodine, 113° , to a eutectic point at 80.5° and 21 mol. per cent. of the iodide; on further increasing the iodide, the freezing point remains practically constant, though there are indications of a second maximum at 82° . This is probably an example of the freezing-point curve of dissociating compounds where, according to Kremann (Abstr., 1905, ii, 76), the maximum is often very flat and the eutectics solidify about the same temperature. From these results no definite conclusions as to the presence of chemical compounds can be drawn.

The tendency to the formation of higher polyiodides increases in the order (Li, Na), K, NH_4 , Rb, Cs, which is the same as the order of the metals in the periodic system and of the decrease in solubility of the platinichlorides and other slightly soluble salts. G. S.

Simple Process for the Continuous Electrolytic Preparation of Potassium Chlorate. A. WALLACH (*Zeit. Elektrochem.*, 1906, 12, 667—668).—Into a large beaker with concentric cylinders of platinum gauze for electrodes and a mechanical stirrer, is placed a solution containing 25 grams of potassium chlorate, 0.2 gram of potassium chromate, and 0.8 c.c. of concentrated hydrochloric acid in 100 c.c.; a current density of 0.15 ampere per sq. cm. is used. Fresh solution is dropped in to replace the decomposed chloride and make up for the

loss of water by evaporation. The chlorate crystals are removed every twenty-four hours. In a ninety hour run the yield was 92 per cent.

T. E.

Electrolysis of Potassium Nitrate. CHARLES COUCHET R. C. SCHLOSSER, and LOUIS DUPARC (*Zeit. Elektrochem.*, 1906, 12 665—666).—When fused potassium nitrate is electrolysed, either with direct or alternating current, potassium nitrite and oxide are formed, the metallic electrodes being oxidised at the same time. The best yield of nitrite is obtained with graphite electrodes. The yield increases as the temperature is raised and the current density increased; it is much better with direct than with alternating current. The gases evolved consist mainly of carbon dioxide and nitric oxide, with smaller quantities of oxygen and nitrogen.

T. E.

Organosols and Gels of Sodium Chloride. CARL PAAL and GUSTAV KÜHN (*Ber.*, 1906, 39, 2859—2862. Compare this vol., ii, 351).—The precipitate obtained by the addition of light petroleum to the benzene solution of the condensation product of ethyl chloroacetate and ethyl sodiomalonate, is completely soluble in benzene when freshly prepared, but loses this property when dried in a vacuum. It contains 58 per cent. of sodium chloride.

Similar results are obtained when the condensation occurs in xylene solution.

With acetyl chloride and ethyl sodiomalonate in presence of benzene, a clear solution is first obtained, but this rapidly deposits a gel, which, when dry, contains 87.27 per cent. of sodium chloride.

Acetyl chloride and ethyl sodioacetonedicarboxylate yield a gel containing 95.62 per cent. of sodium chloride.

J. J. S.

Organosols and Gels of Sodium Bromide. CARL PAAL and GUSTAV KÜHN (*Ber.*, 1906, 39, 2863—2866. Compare this vol., ii, 351, and preceding abstract).—When ethyl bromoacetate, acetyl bromide, or phenacyl bromide is condensed with ethyl sodiomalonate in the presence of benzene, a colloidal solution is obtained, from which light petroleum precipitates an adsorption compound of colloidal sodium bromide with organic substances. The organosols of sodium bromide are less stable than those of sodium chloride, and are more readily transformed into the corresponding gels. A partial conversion into crystalline sodium bromide also occurs in the presence of small amounts of water. It has not been found possible to obtain organosols or gels containing sodium iodide, as in organic condensations in the presence of benzene this salt separates in a crystalline form.

J. J. S.

Electrolytic Production of Sodium Persulphate. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE & ERICH MÜLLER (D.R.-P. 172508).—Sodium persulphate may be conveniently prepared by dissolving Glauber's salt (150 parts) in 70 parts of concentrated sulphuric acid and electrolysing at 17° with a current density of 0.2 ampere per square cm. of anode, and 4 amperes per square cm. of cathode; the persulphate is readily deposited, for, although water can dissolve

50 per cent. of the salt, only about 6 per cent. is taken up by the strong sulphuric acid solution. G. T. M.

Mixed Crystals of Anhydrous Sodium Sulphate, Tungstate, and Molybdate. H. E. BOEKE (*Zeit. anorg. Chem.*, 1906, 50, 355—381).—An account is given of the investigation of a ternary system in which mixed crystals occur; the theory of these systems has recently been developed by Schreinemakers (*Abstr.*, 1905, ii, 154, 376, 685).

Anhydrous sodium sulphate melts at 888° and has a transition point $\alpha - \epsilon$ at 239° . Sodium tungstate melts at 698° and shows two transition points, $\beta - \gamma$ at 588° and $\gamma - \delta$ at 564° . Sodium molybdate melts at 692° , and has at least three transition points, $\alpha - \beta$ at 619° , $\beta - \gamma$ at 587° , and $\gamma - \delta$ at 431° . The designation of the different forms is chosen from the behaviour of the three salts in the binary systems.

From the results of thermal measurements, confirmed by microscopic observations, it is shown that the binary system, $\text{Na}_2\text{SO}_4 - \text{Na}_2\text{MoO}_4$, forms a continuous series of mixed crystals on solidification, whilst the systems $\text{Na}_2\text{WO}_4 - \text{Na}_2\text{SO}_4$ and $\text{Na}_2\text{MoO}_4 - \text{Na}_2\text{WO}_4$ form two series of mixed crystals which are isodimorphous. There is a minimum in the freezing-point curve of each of the three binary systems.

In the ternary system, the composition is represented on an equilateral triangle, the temperature axis being perpendicular to the plane of the latter, so that the temperatures of the beginning and end of crystallisation are represented by a pair of surfaces which meet in three points belonging to the respective binary systems. Similar pairs of surfaces determine the equilibria for transitions in ternary mixed crystals. As the molybdate and tungstate show a very analogous behaviour, the points of the surfaces were determined in mixtures produced by addition of gradually increasing amounts of the sulphate to mixtures of the other two in varying proportions.

From the fused mass, two series of ternary mixed crystals separate, there being a gap over part of the surface of fusion. The transition phenomena in the ternary system correspond in general with those in the three binary systems. It could not be definitely determined whether a ternary minimum was present. G. S.

Atomic Weight of Silver. PHILIPPE A. GUYE and G. TER-GAZARIAN (*Compt. rend.*, 1906, 143, 411—413).—The generally accepted value 107.93 for the atomic weight of silver due to Stas, and obtained from the ratios $\text{KClO}_3 : \text{KCl}$ and $\text{Ag} : \text{Cl}$, is higher than the mean value 107.89 obtained by other methods (*Abstr.*, 1906, ii, 19); the authors have therefore examined potassium chlorate for impurities of potassium chloride or hypochlorite, and find that, whilst even the crude commercial salt is free from the latter impurity, the former is always present to the extent of from 0.022 to 0.029 per cent. in the most carefully recrystallised specimens of the chlorate. Clarke's value for the atomic weight of silver deduced from all the determinations involving the ratios $\text{KClO}_3 : \text{KCl}$ and $\text{KCl} : \text{Ag}$ is 107.927, and this becomes 107.879 when corrected for the amount of potassium chloride

present in the chlorate; and Marignac's value from the ratio $\text{AgClO}_3 : \text{AgCl}$, combined either with the ratio $\text{Cl} : \text{H}$ (Dixon and Edgar, *Abstr.*, 1905, ii, 696), or the ratio $\text{Ag} : \text{AgCl}$ (Richards and Wells, *Abstr.*, 1905, ii, 450) is 107.902. The mean value for the atomic weight of silver, obtained by ten different methods, is therefore 107.890, with an upper and lower limit of 107.908 and 107.871 respectively ($\text{O} = 16$).
M. A. W.

Silver and Silver Sulphide. K. FRIEDRICH and A. LEROUX (*Metallurgie*, 1906, 3, 361—371).—The freezing-point curve of mixtures of silver and silver sulphide has been determined. The depression of the freezing point of silver by the addition of small quantities of silver sulphide is in agreement with that calculated theoretically. At 906° a separation into two layers takes place. The eutectic mixture, which is almost pure silver sulphide, solidifies at 806° . A development of heat, increasing with the percentage of silver sulphide, is also observed at 175° , and corresponds with a transformation of silver sulphide in the solid state. Silver sulphide may be detected microscopically in silver even when present only to a very small extent. This test may be made more sensitive by exposing the polished specimens to the action of strong light. In the presence of even 0.01 per cent. of silver sulphide, the silver assumes brilliant interference tints, owing to the formation of a thin film of sulphide. Silver selenide and telluride are not sensitive to light.

The formation of capillary silver in the fusion of silver sulphide takes place even when precautions are taken to exclude water vapour. The presence of occluded gas is also not necessary. The first appearance of capillary silver is observed slightly above 175° , and the phenomenon is possibly connected with the transformation of silver sulphide at this temperature.
C. H. D.

Ammonium Syngenite. JOH. D'ANS (*Ber.*, 1906, 39, 3326—3328. Compare Bell and Taber, this vol., ii, 352).—Ammonium calcium sulphate, which is readily prepared in glistening, silky needles by adding calcium sulphate to an almost saturated solution of ammonium sulphate and, after some days, washing the product with 50 per cent. alcohol, has the composition $\text{Ca}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, analogous to potassium calcium sulphate, and is stable at 25° . A comparison of solubility curves for ammonium calcium sulphate at 25° and 50° (Bell and Taber, *loc. cit.*) shows that the transformation point of ammonium syngenite lies below 0° .
G. Y.

System Lime, Gypsum, Water, at 25° . FRANK K. CAMERON and JAMES M. BELL (*J. Amer. Chem. Soc.*, 1906, 28, 1220—1222).—The composition has been determined of solutions which were prepared by adding: (1) solid gypsum to solutions of lime of various strengths; and (2) lime to solutions of gypsum of various strengths, and keeping the mixtures agitated for two weeks at 25° . The results are tabulated and plotted as curves. It is found that the solubility of lime in gypsum solutions is nearly constant, but is slightly greater in the more con-

centrated solutions. In lime solutions, however, the solubility of gypsum decreases regularly as the amount of lime in solution increases.

E. G.

Phosphates of Calcium. III. Superphosphate. FRANK K. CAMERON and JAMES M. BELL (*J. Amer. Chem. Soc.*, 1906, 28, 1222—1229. Compare Cameron and Seidell, *Abstr.*, 1905, ii, 33; 1906, ii, 163; and Cameron and Bell, *Abstr.*, 1906, ii, 164).—A study has been made of the solubility curves in the four-component system, lime, phosphoric acid, sulphuric acid, water, at 25°. The solid phases which are present at several points on the curves are stated in tabular form. Determinations have also been made of the conditions obtaining at other temperatures.

The results of the action of water on a superphosphate composed of gypsum and monocalcium phosphate at 25° are as follows. The addition of water to monocalcium phosphate crystals causes a partial change to dicalcium phosphate and the formation of a solution saturated with respect to both phosphates. A small amount of gypsum is also dissolved. On the addition of a further quantity of water, the monocalcium phosphate disappears and dicalcium phosphate is produced. The effect of this treatment is to wash out some phosphoric acid, together with considerable quantities of calcium and a very small amount of gypsum. On removing some of the solution and adding more water to the residue, the crystalline dicalcium phosphate gives up phosphoric acid, which carries some of the phosphate into solution. The solid residue changes to a solid solution of lime and phosphoric acid, and, on continued treatment with water, this solid solution changes gradually into that solid solution which, in saturated gypsum solutions, dissolves unchanged, that is, the ratio of lime and phosphoric acid which enter solution is the same as in the solid solution. At this stage, the gypsum has a much greater solubility, and will probably be all washed away before the solid solutions have entirely disappeared. Finally, the comparatively insoluble solid solution of lime and phosphoric acid, which contains relatively more lime than is required by the formula $\text{Ca}_3(\text{PO}_4)_2$, will gradually be dissolved.

E. G.

Action of Ammonia on Strontium. Strontium-ammonium. G. ROEDERER (*Bull. Soc. chim.*, 1906, [iii], 35, 715—727).—Experimental details are given of the results already recorded (*Abstr.*, 1905, ii, 455). When strontium-ammonium is exposed under reduced pressure, it decomposes slowly at 20°, and very rapidly above this temperature, evolving a mixture of ammonia and hydrogen and leaving a white mass of strontiamide, $\text{Sr}(\text{NH}_2)_2$. When a solution of strontium-ammonium is treated with carbon monoxide at -45°, a dull yellow, pulverulent mass of *strontium carbonyl*, $\text{Sr}(\text{CO})_2$, is obtained; this becomes bright yellow on exposure to moist air, forms a limpid, yellow solution with water, and blackens when heated under reduced pressure, yielding a mixture of strontia, strontium carbonate, and carbon.

By the action of oxygen on strontium-ammonium, dissolved in ammonia solution, cooled to -55°, the deep bluish-black colour lightens and finally disappears, and, on allowing the ammonia to evaporate, a

mixture of strontia and strontium dioxide is obtained (compare Mentrel, *Abstr.*, 1903, ii, 77). Nitrogen dioxide also reacts with strontium-ammonium, dissolved in ammonia solution, forming strontium hyponitrite.

When dry ammonia is passed over strontium heated at 200° , hydrogen and nitrogen are obtained, and some strontiamide is formed. At 800° , the yellowish-grey product obtained is a mixture of strontium hydride and nitride.

T. A. H.

Gelatinous Inorganic Salts of the Alkaline Earth Metals.

CARL NEUBERG and ERNST NEIMANN (*Chem. Centr.*, 1906, ii, 590—591; from *Biochem. Zeit.*, 1, 166—176).—When dilute sulphuric acid is added to a methyl-alcoholic solution of barium hydroxide, barium sulphate is precipitated in a gelatinous form. It can be dried in a vacuum and heated strongly without change, but on boiling with water for a considerable time it passes into the ordinary form; this change is accelerated by the addition of hydrochloric acid.

Barium hydrogen phosphate can be obtained in a similar gelatinous modification.

If a current of carbon dioxide is passed into a saturated methyl-alcoholic solution of barium oxide, the liquid is suddenly transformed into a solid jelly which, when freed from solution, represents a gelatinous form of barium carbonate. By the introduction of more carbon dioxide, a white powder of the composition $\text{BaCO}_3 \cdot \text{H}_2\text{O}$ is obtained, which is readily soluble in water. The solution after a time deposits a flocculent precipitate. Both forms of the carbonate dissolve slowly in methyl alcohol. The methyl-alcoholic solutions are colloidal in appearance and very viscous: barium sulphate is precipitated on addition of sulphuric acid, but the methyl alcohol can be removed by distillation without alteration of the colloidal character. Addition of excess of water causes precipitation, and gelatinous barium oxalate separates on addition of a solution of oxalic acid.

When ethyl alcohol and a little water are added to a methyl-alcoholic solution of barium oxide, the hydrate, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, crystallises in well-formed needles. If the solution is slowly evaporated in a vacuum, barium methoxide, $\text{Ba}(\text{OMe})_2$, separates in transparent needles. It is slightly soluble in ethyl alcohol, insoluble in ether and acetone.

On addition of an alcoholic solution of potassium hydrogen sulphide, hydrated barium sulphide, $\text{BaS} \cdot \text{H}_2\text{O}$, separates out in a gelatinous condition; it dissolves slowly in contact with methyl alcohol. Gelatinous modifications of barium thiocyanate and tannate, and of various calcium, strontium, and magnesium compounds, have been prepared by similar methods. The stability of these compounds increases with increasing molecular weight.

H. M. D.

Behaviour of Barium and Calcium Carbonates at High Temperatures. H. E. BOEKE (*Zeit. anorg. Chem.*, 1906, 50, 244—248).—According to Le Chatelier (*Abstr.*, 1887, 431), barium carbonate melts in an open vessel at 795° , whilst Finkelstein (this vol., ii, 354) has recently shown that the undecomposed carbonate does

not fuse even at 1350° . The author, in agreement with Finkelstein, finds that the salt only partially fuses when heated at 1380° in a current of carbon dioxide, and considers that the lower fusing point in an open vessel indicates the formation of a basic salt. It has also been found that the salt has a transition point at 811° when heated in a current of carbon dioxide.

When aragonite is heated to 470° , it changes into calcite, and this transition takes place at lower temperatures (445°) on long-continued heating. The change is not accompanied with an appreciable development of heat.

Le Chatelier (Abstr., 1893, ii, 119, 166) claims to have melted calcium carbonate under a pressure of 1000 kilos. per sq. cm. at a temperature a little below the melting point of gold (1064°), but other investigators have thrown doubt on this observation. The author now finds that the salt does not melt when heated to 1400 – 1500° under a pressure of carbon dioxide of 30 atmospheres, although the original fine powder becomes crystalline; in these circumstances partial dissociation into calcium oxide and carbon dioxide also takes place.

G. S.

Contamination of Zinc and its Compounds with Lead.

T. TUSTING COCKING (*Chemist and Druggist*, 1906, 69, 507. Compare Hill, Abstr., 1905, ii, 356).—The lead was estimated as sulphate, as chromate, and colorimetrically as sulphide. Commercial zinc was found to contain 0.4–1.6 per cent., the "arsenic-free" metal 0.016–0.1 per cent. of lead. Zinc oxide contains 0.05–0.4 per cent., the carbonate 0.04–0.14 per cent. of lead; none of the other zinc salts examined contained more than 0.1 per cent.

G. S.

Precipitated Basic Carbonates of Zinc and Cadmium.

MORITZ KOHN (*Zeit. anorg. Chem.*, 1906, 50, 315–317).—Precipitated basic carbonate of zinc completely precipitates solutions of ferric chloride, aluminium nitrate, and uranyl nitrate in the cold, whilst chromic nitrate is only partially precipitated in the cold, but completely on heating. The precipitate from the uranium solution consists of hydrated uranic acid slightly contaminated with zinc.

Precipitated cadmium nitrate precipitates completely solutions of ferric chloride and nitrate, but acts only slightly on solutions of chromium, uranyl, and aluminium nitrates in the cold.

G. S.

Determination of the Atomic Weights of the Elements of the Rare Earths.

WILHELM FEIT and KARL PRZIBYLLA (*Zeit. anorg. Chem.*, 1906, 50, 249–264. Compare Abstr., 1905, ii, 250).—It is pointed out that the sulphate method for determining the atomic weights of the metals of the rare earths is very troublesome, and an alternative method, which is very simple and accurate, is suggested. A known weight of the oxide is dissolved in $N/2$ sulphuric acid and titrated back with $N/10$ alkali, methyl-orange being used as indicator. For the method to be applicable it is necessary that the normal sulphates should be absolutely neutral towards the indicator, and it is shown that in certain typical cases this condition is fulfilled.

The atomic weights of a number of the rare earth elements have been determined by this method; the oxides employed were prepared by the authors, or obtained from other workers in the same field, and were spectroscopically pure. The results, corrected to a vacuum, are as follows: La=139.17; Pr=140.62; Nd=144.6; Sm=150.56; Eu=152.66; Gd=157.47; Yb=173.52; Yt=89.40. With two exceptions, the results are in excellent agreement with the most trustworthy previous determinations; the value for europium is 0.63 unit higher than that obtained by Urbain; that for yttrium is also higher.

The authors do not claim extreme accuracy for these observations, which were carried out in a technical laboratory, but consider that the method avoids certain difficulties of the sulphate method, and is capable of giving results of the highest accuracy. G. S.

Electrolytic Precipitation of Lead from Acetate Solutions.

RALPH C. SNOWDON (*J. Physical Chem.*, 1906, 10, 500—501).—By using a revolving cathode and a low current density it is possible to deposit lead from a solution of its acetate in the form of a crystalline adherent film. The adherent character of the deposit is improved by the addition of a little gelatin to the solution. W. A. D.

Lead Matte. HUGO WEIDMANN (*Metallurgie*, 1906, 3, 660—664).—Mixtures of lead sulphide and ferrous sulphide, prepared by fusion in an electric furnace, were examined. Pure ferrous sulphide melts at 1137°, and lead sulphide at 970° (compare Friedrich and Leroux, this vol., ii, 355). The freezing-point curve of mixtures of the two sulphides consists of two branches, meeting at a eutectic point at 782° and 25.8 per cent. of ferrous sulphide. Compounds of the two sulphides are therefore not formed, and the fact that the eutectic horizontal is to be traced as far as the limits of the diagram proves that solid solutions do not occur. These conclusions are confirmed by microscopic examination of the solidified mixtures. C. H. D.

Modifications of Lead Oxide. RUDOLF RUER (*Zeit. anorg. Chem.*, 1906, 50, 265—275. Compare this vol., ii, 542).—The author has observed that some specimens of pure lead oxide have a brownish-yellow colour, which, on heating to 600° and allowing to cool, becomes light yellow. The latter modification again becomes brownish-yellow on prolonged rubbing in a mortar with considerable pressure, and on further heating and cooling the yellow colour is restored.

Geuther (Abstr., 1884, 824) has shown that by boiling lead hydroxide with 10 per cent. sodium hydroxide solution, a light yellow modification, and with very concentrated hydroxide solution a red modification, of lead oxide is obtained. It has now been found that the red oxide is changed to the yellow by heating at 700°, but the transition is slower than in the case of the reddish-brown oxide referred to above. Further, the light yellow oxide is considerably more soluble in water than the red modification.

On the basis of these observations, it is suggested that the light yellow oxide is unstable at the ordinary temperature, the change to a more stable form being accelerated by friction and pressure; at higher

temperatures (above 500—600°) the yellow is the stable modification. It remains for the present undecided whether Geuther's red oxide and that obtained from the yellow by rubbing are identical; they appear to differ in the readiness with which they undergo transition on heating, and the yellowish-brown oxide is about as soluble in water as the light yellow variety, and, therefore, much more soluble than the red oxide, but the latter property may be due to the presence of a considerable proportion of the light yellow in the yellowish-brown oxide.

G. S.

New Method of preparing Lead Peroxide. LOUIS FRIDERICH, EDOUARD MALLET, and PHILIPPE A. GUYE (*Chem. Centr.*, 1906, ii, 465; from *Mon. Sci.*, 1906, [iv], 20, ii, 514—518).—A mixture of five kilos. of lead sulphate with 1.2 kilos. of magnesium oxide is suspended in 13 litres of hot water, and the whole is then saturated with chlorine under pressure. The liquid portion is run off, and the lead peroxide is washed with water. In order to remove traces of chloride and sulphate, as well as any lead monoxide, the crude peroxide is treated first with boiling 10 per cent. sodium hydroxide and then with hot nitric acid. The resulting product contains 97 per cent. of peroxide. The reaction may be represented by the two equations $\text{PbSO}_4 + \text{MgO} = \text{MgSO}_4 + \text{PbO}$ and $\text{PbO} + \text{MgO} + \text{Cl}_2 = \text{PbO}_2 + \text{MgCl}_2$.

P. H.

Electrolytic Corrosion of the Bronzes. B. E. CURRY (*J. Physical Chem.*, 1906, 10, 474—499).—The rates of corrosion of bronzes of different composition were determined in aqueous solutions of different salts, when the bronze was made the anode and a platinum wire the cathode; the proportion of copper in the bronzes varied from 95 per cent. to 5 per cent., with 5 per cent. intervals. Usually a 7 per cent. solution of the salt was employed, the following solutions being used: sodium sulphate, sodium nitrate, sodium acetate, sodium carbonate, alkaline sodium tartrate, ammonium oxalate containing oxalic acid, sodium chloride, sodium persulphate, ammonium sulphate, and copper sulphate. A current of about 25 milliamperes and a current density of 0.18 ampere per square decimetre were employed. Curves are drawn showing the variation of current efficiency with the composition of the alloy, and the nature of the solid phases in the latter. The conclusions are summarised as follows.

The α -bronzes corrode more rapidly than any others, almost pure copper dissolving; from the $\alpha + \delta$ - and $\alpha + \beta$ -alloys, copper dissolves more rapidly than tin. The β , δ , $\beta + \gamma$, $\delta + \text{Cu}_3\text{Sn}$, $\text{Cu}_3\text{Sn} + \epsilon$, and ϵ -bronzes undergo very little change and tend to become passive. The $\epsilon + \text{Sn}$ bronzes become rich in copper on the surface, and tend to disintegrate as the tin dissolves. The cause of certain of the bronzes becoming passive appears to be the formation of a film of stannic oxide; the film was obtained in quantity and examined. The ϵ -bronze is most resistant to corrosion. No bronze becomes passive in solutions of chlorides, a high current efficiency being observed whatever be the composition of the bronze. In all other salts the curve of current efficiency shows well-marked fields, an abrupt change in the rate of corrosion occurring at the appearance or disappearance of a phase in the equilibrium diagram.

The effects of chemical corrosion were in most cases found to be similar in nature to those of electrolytic corrosion. W. A. D.

Stable Cupric Hydroxide and the Basic Salt $7\text{CuO}\cdot 2\text{SO}_3\cdot 5\text{H}_2\text{O}$ (Brochantite). JOSEF HABERMANN (*Zeit. anorg. Chem.*, 1906, **50**, 318—319).—A fairly stable hydroxide of copper, $\text{Cu}(\text{OH})_2$ (already obtained by Böttger, *J. pr. Chem.*, 1858, **73**, 491), can be prepared by digesting basic copper sulphate, $7\text{CuO}\cdot 2\text{SO}_3\cdot 5\text{H}_2\text{O}$, with 10 per cent. potassium hydroxide solution, washing the precipitate with cold water and alcohol, and drying at 100° . It is light bluish-green in colour.

The basic sulphate itself is obtained by the action of 50 c.c. of 2*N*-sodium hydroxide on a solution of 5 grams of copper sulphate in 200 c.c. of water in the cold; it is washed and dried at 100° . G. S.

The Two Forms of Mercuric Iodide. LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 192. Compare Kastle and Clark, *Abstr.*, 1900, ii, 141; Kastle and Reed, *Abstr.*, 1902, ii, 324; Gernez, *Abstr.*, 1903, ii, 428, 481).—The solubility of mercuric iodide in nitrobenzene, *m*-nitrotoluene, *p*-nitrotoluene, and α -nitronaphthalene has been studied in the following way. Known quantities of the iodide were added successively to the solvent, which, after heating to cause the salt to dissolve, was cooled until crystals of the iodide began to separate; at this point the temperature was observed. In order to obviate supersaturation, a crystal of the iodide was added just before the point of separation was reached; readings were taken both when the yellow and the red forms of the iodide were added. Only one value for the solubility was observed in either case at a definite temperature; between temperatures of 0° and 220° , the curves of solubility of the iodide are continuous in the case of all the solvents used, no break in the direction being observed at the transformation point of the iodide (about 130°). Above 130° , only the yellow form separates in all cases; below this temperature the yellow form separates first, and is persistent for a length of time depending on the distance of the temperature below the transition point. As the curve below 130° is continuous with that above 130° , it appears that the yellow form only exists in solution at all temperatures. W. A. D.

Chromates of Mercury, Bismuth, and Lead. ALVIN J. COX (*Zeit. anorg. Chem.*, 1906, **50**, 226—243. Compare Abegg and Cox, *Abstr.*, 1904, ii, 563, 662).—The conditions under which the chromates of lead, mercury, and bismuth are capable of existing in solution, and the limits of their existence, have been determined. In accordance with the phase rule, each of these salts has a definite hydrolytic pressure, in other words there is a certain minimum concentration of acid below which the salt cannot exist. By solubility determinations the respective concentrations have been ascertained, and it has then been found possible to isolate the pure salts.

Two chromates of mercury, HgCr_2O_7 and HgCrO_4 , have thus been prepared; at 25° they are in equilibrium with solutions containing 10.46 and 0.46 gram-mols. of chromic acid per litre respectively. The

former is a deep carmine-red powder; the latter a light orange powder. The two lead salts, PbCr_2O_7 and PbCrO_4 , are in equilibrium with solutions containing 6.87 and 0.00002 gram-mols. of the acid respectively. The former salt occurs as a lustrous, red, crystalline powder. The bismuth salts, $\text{Bi}_2\text{O}_3\cdot\text{CrO}_3$ and $\text{Bi}_2\text{O}_3\cdot 2\text{CrO}_3$, are in equilibrium with solutions containing 7.80 and 0.00001 gram-mols. of the acid respectively; the former is an orange-scarlet, the latter an orange-yellow powder.

Salts whose hydrolytic pressure is greater than the solubility of the acid at the temperature of experiment cannot, of course, be obtained in this way. It has been found that a solution saturated at 25° contains 10.8 gram-mols. of chromic acid per litre.

Many salts intermediate in composition to the respective pairs of compounds are mentioned in the literature, but they must be regarded as mixtures.

G. S.

Determination of the Melting Points of Lead-aluminium and Bismuth-aluminium Alloys by means of Thermo-electric Pyrometers. HECTOR PÉCHEUX (*Compt. rend.*, 1906, 143, 397—398. Compare Abstr., 1904, ii, 564; 1905, ii, 526; this vol., ii, 286).—The author has determined the solidifying points of aluminium, and of certain of its alloys, with lead and bismuth by means of two thermo-electric couples, one composed of nickel and copper, the other of platinum and 10 per cent. platinum-iridium; the absolute error for the range of temperature employed (630 — 720°) is 0.71° for the former and 2.75° for the latter couple, and, provided that precautions are taken to avoid oxidation, and the Thomson effect, the nickel-copper pyrometer is more suitable for industrial purposes than the platinum-iridium couple.

M. A. W.

Constituents of Manganese-molybdenum Alloys. G. ARRIVAUT (*Compt. rend.*, 1906, 143, 464—465).—Manganese-molybdenum alloys richer in molybdenum than those already described (this vol., ii, 676), prepared by reducing the mixed oxides with aluminium powder, form hard, brittle, homogeneous ingots, silver-white in colour, non-magnetic, readily soluble in hot concentrated nitric or sulphuric acid, or fused alkali hydrogen sulphites. The alloys consist of free manganese associated with one or other of the compounds Mn_2Mo , MnMo , or MnMo_2 , which form crystalline, metallic powders, steel-grey in colour and non-magnetic. The compound Mn_2Mo is left as a residue when alloys containing 35.11 to 43.94 per cent. of molybdenum are treated with a 10 per cent. alcoholic solution of acetic acid; it has a sp. gr. 8.37 at 0° , the calculated value being 7.91. The alloy MnMo is similarly isolated by the action of dilute hydrochloric acid from alloys containing 43.57 to 59.25 per cent. of molybdenum; it has a sp. gr. 8.60 at 0° , the calculated value being 8.23. The compound MnMo_2 is obtained by treating alloys containing 64.70 to 72.27 per cent. of molybdenum with concentrated hydrochloric acid; it has a sp. gr. 8.70 at 0° , the calculated value being 8.59. All the compounds are attacked by chlorine at the ordinary temperature or with incandescence at 300° , by oxygen or sulphur at a red heat, and by water vapour at

250°, whilst hydrochloric or hydrofluoric acid only dissolve the compound Mn_2Mo .
M. A. W.

Use of Metallic Deposits in the Micrographical Examination of Alloys. FEDERICO GIOLITTI (*Gazzetta*, 1906, **36**, ii, 142—147).—A preliminary note pointing out the advantages of depositing electrolytically a thin film of metal on the section of steel or bronze which is to be examined micrographically. The thin film of metal is subsequently removed by polishing with finely levigated rouge; the electrolytic treatment greatly emphasises the characteristic micro-structure in the case of different kinds of steel and bronze. Either copper, nickel, or silver may be chosen as the metal to be deposited on the alloy.
W. A. D.

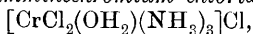
Iron and Calcium. OLIVER P. WATTS (*J. Amer. Chem. Soc.*, 1906, **28**, 1152—1155).—Experiments are described which were carried out with the object of preparing alloys by fusing mixtures of iron and calcium in a graphite crucible by means of an electric resistance furnace. No alloys were formed, but the iron became richer in carbon and silicon. It is supposed that the silicon was derived from silica present in the magnesia lining of the crucible, and the carbon from carbon monoxide formed during the operation. When a thin piece of ignited calcium is plunged into a jar of carbon dioxide, calcium oxide, calcium carbide, and carbon are produced. Other attempts to obtain alloys were made by heating calcium in a pure iron cylinder at 850—880°, and by reducing iron oxide with calcium filings in presence of excess of calcium, but without success.

Experiments were also made to ascertain whether phosphorus and sulphur contained in iron could be removed by heating the metal with calcium. It was found that in one case the whole of the sulphur present was removed and in another case that the percentage of phosphorus in the iron was reduced from 1.96 to 1.56. The commercial application of calcium to the removal of phosphorus from iron is impracticable. [Compare Quasebart, this vol., ii, 229; Stockem, *ibid.*, ii, 285.] E. G.

Copper Steels. PIERRE BREUIL (*Compt. rend.*, 1906, **143**, 377—380. Compare this vol., ii, 546, 677).—The mechanical properties of three series of copper steels have been examined, and the values of the breaking load, the torsion, and the hardness of fourteen samples are tabulated in the original. The fragility of the steels as determined by the breaking load is not much increased by the copper, and none of the steels containing 0.5 to 4 per cent. of copper are brittle; the elastic limit is considerably augmented by the copper, and the hardness of the steels is generally higher than that of nickel steels containing the same amount of carbon which have received the same thermal treatment.

The corrosive action of dilute sulphuric acid on copper steels is less than on steels of the same carbon content not containing copper. Copper steels containing from 0.5 to 4 per cent. of copper are characterised by a fine structure, and when examined under the microscope exhibit a perlite structure which becomes more marked as the percentage of copper increases.
M. A. W.

Triammine Chromium Salts. A Contribution to the Chemistry of Hydrates. V. Chromium Compounds. ALFRED WERNER (*Ber.*, 1906, **39**, 2656—2667. Compare this vol., i, 816; ii, 452).—*Dichloroaquatriamminechromium chloride*,



formed by treating Wiede's triamminechromium¹ tetroxide (compare Hofmann and Hiendlmaier, *Abstr.*, 1905, ii, 716) with concentrated hydrochloric acid in the presence of glacial acetic acid, is purified by conversion into the nitrate, the chloride being regenerated by hydrochloric acid at 0°. It crystallises in violet-brown leaflets and is easily soluble in water to a blue solution.

The *nitrate*, $[\text{CrCl}_2(\text{OH}_2)(\text{NH}_3)_3]\text{NO}_3$, obtained from the crude chloride and nitric acid, separates from dilute nitric acid in a felted mass of bluish-grey needles.

The *sulphate*, $[\text{CrCl}_2(\text{OH}_2)(\text{NH}_3)_3]\text{SO}_4$, crystallises in reddish-blue needles. The *iodide*, $[\text{CrCl}_2(\text{OH}_2)(\text{NH}_3)_3]\text{I}$, forms a greenish-blue, crystalline powder. The *basic iodide*, $[\text{Cr}(\text{OH}_2)_3(\text{NH}_3)_3](\text{OH})\text{I}_2$, separates on the addition of solid potassium iodide to the crude chloride dissolved in a mixture of water and pyridine. The salt retains pyridine, which is removed by repeated trituration with a saturated solution of potassium iodide. It crystallises in bluish-red leaflets, and is soluble in water. The *bromide*, $[\text{Cr}(\text{OH}_2)_3(\text{NH}_3)_3]\text{Br}_3$, is obtained from a solution of the basic iodide and concentrated hydrobromic acid at 0°; it forms reddish-brown crystals, and is very hygroscopic. C. S.

Trichlorotriamminecobalt and its Hydrates. ALFRED WERNER [and EMIL BINDSCHEDLER] (*Ber.*, 1906, **39**, 2673—2679. Compare *Abstr.*, 1905, ii, 93).—The first and the last members of the series $\text{CoCl}_3(\text{NH}_3)_3$, $[\text{CoCl}_2(\text{OH}_2)(\text{NH}_3)_3]\text{Cl}$, $[\text{CoCl}(\text{OH}_2)_2(\text{NH}_3)_3]\text{Cl}_2$, $[\text{Co}(\text{OH}_2)_3(\text{NH}_3)_3]\text{Cl}_3$, have been prepared. The source of the first-mentioned compound is a substance, obtained from dichloroaquatriamminecobalt chloride (dichro-salt) and sodium hydroxide, which is to be described fully in a subsequent paper. The substance is triturated with concentrated hydrochloric acid, whereby dichloroaquatriamminecobalt chloride and *trichlorotriamminecobalt*, $\text{CoCl}_3(\text{NH}_3)_3$, are obtained, only the latter remaining after twenty-four hours' washing with water. It dissolves slowly in cold water, forming the hydrated compounds, and nitric or sulphuric acid precipitates from the solution the salt of dichloroaquatriamminecobalt. The substance is unchanged by trituration with nitric acid, and the chlorine is in the non-ionised state.

Triaquatriamminecobalt chloride, $[\text{Co}(\text{OH}_2)_3(\text{NH}_3)_3]\text{Cl}_3$, is formed when trinitratotriamminecobalt (Jørgensen, *Ber.*, 1882, **15**, 1900) is treated for twenty-four hours with very dilute acetic acid, and the solution treated with hydrochloric acid at 0°. It forms a heavy, reddish-violet, crystalline powder. The corresponding bromide is prepared in a similar manner. In both compounds the halogen is wholly removed by silver nitrate. C. S.

Action of Liquid Ammonia on Certain Metallic Anhydrides [Acidic Oxides]. ARTHUR ROSENHEIM and FELIX JACOBSON (*Zeit. anorg. Chem.*, 1906, **50**, 297—308).—Up to the present the existence

of amino- or imino-derivatives of weak electro-negative elements has not been definitely established. Certain compounds of the latter type have now been obtained by the action of liquid ammonia on the anhydrides and chlorine derivatives of certain quinquivalent and sexavalent metals.

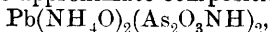
Experiments with the liquefied gas were carried out mainly as described by Stock and Hoffmann (Abstr., 1903, ii, 207). The compounds were not brought into contact with water, but were washed with liquid ammonia, and the omission of this precaution explains the unsatisfactory results obtained by previous observers in this field.

Chromium Compounds.—By the action of liquid ammonia on chromium trioxide, CrO_3 , in a sealed tube at the ordinary temperature, a brown compound of the empirical formula $\text{CrO}_3 \cdot 3\text{NH}_3$, probably ammonium imidochromate, $\text{NH}:\text{CrO}(\text{O} \cdot \text{NH}_4)_2$, was obtained. It readily gives up ammonia in the air, and dissolves in water to form ammonium dichromate. A lead compound, $(\text{NH}_3)_4(\text{CrO}_3)_2\text{Pb}$, was prepared by interaction of lead iodide, chromium trioxide, and liquid ammonia; it may be regarded as being derived from the imidochromate by replacement of one of the NH_4 groups by lead. Potassium chlorochromate and liquid ammonia interact to form a compound of the formula $\text{K}(\text{NH}_4)\text{CrO}_3\text{NH}$. The formation of the potassium and lead compounds is regarded as confirming the correctness of the suggested constitutional formula for the first-mentioned substance. By the action of ammonia gas on chromyl chloride dissolved in dry chloroform, a voluminous, brown substance, $(\text{NH}_3)_3\text{Cr}_2\text{O}_4(\text{NH}_4)_2$, was obtained; its constitutional formula has not been established.

Molybdenum Compounds.—By the action of liquid ammonia on molybdenum trioxide, MoO_3 , a snow-white compound, $\text{MoO}_3 \cdot 3\text{NH}_3$, was obtained; the same substance is formed by the action of liquid ammonia on molybdenyl chloride. Attempts to establish its constitution did not lead to very conclusive results. A lead salt, probably analogous in composition to the chromium salt already mentioned, was obtained. By the action of potassium amide in liquid ammonia on the trioxide, a practically colourless substance, which appeared to be a mixture of $\text{NH}:\text{MoO}(\text{OK})_2$ and $\text{NK}:\text{MoO}(\text{OK})_2$, was isolated. The first salt is therefore probably ammonium imidomolybdate, $\text{NH}:\text{MoO}(\text{ONH}_4)_2$.

Tungsten and Uranium Compounds.—Tungsten trioxide, WO_3 , does not react with liquid ammonia, even on heating at $108\text{--}109^\circ$ in a sealed tube; with the oxychloride WO_2Cl_2 , a brown compound, $\text{WO}_3 \cdot 3\text{NH}_3$, is obtained. Uranium trioxide does not react with ammonia, but the oxychloride gives a greyish-green precipitate which has not been obtained pure.

Other Compounds.—Arsenic oxide gives with liquid ammonia a white compound of the formula $\text{As}_2\text{O}_5 \cdot 3\text{NH}_3$; its constitution has not been determined. Treated with lead iodide in ammoniacal solution, a heavy, white precipitate, of the approximate composition



is obtained. Antimony pentoxide does not react with ammonia, but the hydrated pentachloride, $\text{SbCl}_5 \cdot \text{H}_2\text{O}$, forms a snow-white, crystalline

powder, not obtained pure. Vanadium pentoxide and ammonia react to form a yellowish-brown, very unstable compound.

No compounds containing the NH_2 group have been obtained.

G. S.

Dihydrate of Molybdic Acid. ARTHUR ROSENHEIM (*Zeit. anorg. Chem.*, 1906, 50, 320. Compare Rosenheim and Davidsohn, *Abstr.*, 1904, ii, 128).—For the preparation of the dihydrate of molybdic acid, 29—30 per cent. nitric acid must be used instead of 20 per cent., as given in the former paper, and the molybdate solution must be added to the nitric acid with stirring, instead of the converse, as previously stated.

G. S.

Compounds of Stannic Sulphate with Alkaline Earth Sulphates and with Lead Sulphate. RUDOLF F. WEINLAND and HUGO KÜHL (*Ber.*, 1906, 39, 2951—2953).—On mixing solutions of orthostannic acid in sulphuric acid and calcium sulphate in the same solvent and concentrating, regularly formed, colourless cubes are obtained of the compound $\text{Sn}(\text{SO}_4)_2 \cdot \text{CaSO}_4 \cdot 3\text{H}_2\text{O}$; similar salts are obtained with barium, strontium, or lead sulphates; they only lose 10 per cent. of their water at 210° , the residue being given off as the compounds decompose, and are therefore regarded as derivatives of orthostannic acid of the type $\text{Sn}[(\text{SO}_4\text{H})_3(\text{OH})_3]\text{M}$, corresponding with Bellucci and Parravano's orthostannates, $\text{X}''\text{Sn}(\text{OH})_6$ (*Abstr.*, 1904, ii, 823; 1905, ii, 40).

E. F. A.

Thorium Hydroxide Hydrosol. ARTHUR MÜLLER (*Ber.*, 1906, 39, 2857—2859. Compare Biltz, *Abstr.*, 1903, ii, 153).—A concentrated hydrosol of thorium hydroxide may be prepared by taking the hydroxide obtained from 20 grams of dry thorium nitrate and, after thoroughly washing with water, boiling with water and adding a solution of 10 grams of nitrate in 50 c.c. of water in quantities of 1 c.c. and boiling for five minutes after each addition. When some 10.2—10.4 c.c. have been added, a slightly opalescent solution is obtained. This can be kept for some time unaltered; it is not affected by boiling, and when evaporated leaves a gelatinous mass which is soluble in water. In other properties it resembles Biltz's hydrosol. Neutral salts produce no precipitate, but small amounts of alkalis, and practically all acids, give a precipitate of the hydroxide.

J. J. S.

Preparation of Ammonium Vanadate and Sodium Uranate. JULIUS OHLY (*Chem. Centr.*, 1906, ii, 465—466; from *Oesterr. Zeit. Berg-, Hüttenwes.*, 1906, 54, 232—234).—Finely-powdered and sifted Utah sandstone containing carnotite is stirred up with hydrochloric, sulphuric, or nitric acid until it assumes a red tint; the mixture is then heated by blowing steam into it until no yellow particles are left in the residue, showing that the vanadium and uranium compounds have gone into solution. The approximately calculated quantity of solid ammonium chloride is now added in portions to the liquid, which, after evaporation to one-third of its volume, is allowed to remain overnight. The crystals of ammonium metavanadate which are deposited are

then recrystallised from a strong solution of ammonium chloride and washed with alcohol. On further evaporation of the mother liquors, a second crop of ammonium metavanadate is obtained. The solution, which is now free from vanadium compounds, is boiled for half an hour with an excess of sodium carbonate and filtered; on adding sodium hydroxide to the filtrate, sodium uranate, Na_2UO_4 , is precipitated.

P. H.

Antimony-cadmium Alloys. WILHELM TREITSCHKE (*Zeit. anorg. Chem.*, 1906, 50, 217—225. Compare Heycock and Neville, *Trans.*, 1892, 61, 888; Kurnakoff and Konstantinoff, *J. Russ. Phys. Chem. Soc.*, 1905, 37, 580).—From an investigation of this system by Tammann's method of thermal analysis, evidence has been obtained of the existence of two compounds of the respective formulæ SbCd and Sb_2Cd_3 , only the first of which is stable.

From all alloys containing 30—100 per cent. of antimony, the compound Sb_2S_3 , containing 42 per cent. by weight of antimony, separates spontaneously; it forms a series of mixed crystals with antimony which are saturated when 53 per cent. by weight of the latter element is present. When alloys containing 42—100 per cent. of antimony are allowed to cool further, there is a sudden considerable development of heat, due in all probability to the formation of the compound SbCd from Sb_2Cd_3 and antimony. The latter compound separates spontaneously in long needles from all alloys containing 0—30 per cent. of antimony, and crystallises also from the fused mass containing 30—100 per cent. of antimony if traces of the solid compound are added. A conglomerate containing Sb_2S_3 and antimony can be obtained at the ordinary temperature by allowing alloys rich in antimony to crystallise spontaneously and suddenly cooling the solid mass when the temperature has fallen to about 400° . The eutectic point Cd—SbCd lies at 292° , and the mixture contains 8 per cent. by weight of antimony; that of SbCd—Sb at 455° and 60 per cent. of the latter element. The eutectic point $\text{Cu}_2\text{Cd}_3\text{—Sb}$ lies at about 410° and 54 per cent. of the latter element.

G. S.

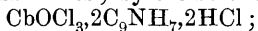
Atomic Weight of Tantalum. FRIEDRICH WILLY HINRICHSSEN and N. SAHLBOM (*Ber.*, 1906, 39, 2600—2608).—The authors have re-determined the atomic weight of tantalum. On repetition of the experiments of Marignac with potassium tantalum fluoride, K_2TaF_7 , which was free from silicon, titanium, and columbium, it was found that the value for the atomic weight of tantalum deduced from the weight of tantalic acid obtained was higher than that deduced from the weight of potassium sulphate obtained. Marignac's method was not considered trustworthy.

Metallic tantalum was converted into the oxide, Ta_2O_5 . As the mean of five determinations, the atomic weight of tantalum was found to be 181.0. This value is distinctly lower than Marignac's.

A. McK.

Preparation of Bismuth Salts. LUDWIG VANINO and F. HARTL (*J. pr. Chem.*, 1906, ii, 74, 142—152. See this vol., i, 785).

Haloid Salts of Columbium Oxychloride (CbOCl_3) and of Columbium Oxybromide. RUDOLF F. WEINLAND and LUDWIG STORZ (*Ber.*, 1906, 39, 3056—3059. Compare Abstr., 1903, ii, 218; 1905, ii, 323, 326).—Double salts of the types $\text{CbOCl}_3 \cdot \text{RCl}$ and $\text{CbOCl}_3 \cdot 2\text{RCl}$, or the corresponding bromides, have been prepared (1) by the addition of RCl or RBr to columbic acid in the concentrated halogen acid, or (2) by the addition of RCl or RBr in alcoholic hydrogen chloride or bromide to an alcoholic solution of columbium oxychloride or oxybromide. By the first method have been obtained $\text{CbOCl}_3 \cdot 2\text{CsCl}$; $\text{CbOCl}_3 \cdot 2\text{RbCl}$; $\text{CbOCl}_3 \cdot \text{C}_9\text{NH}_7 \cdot \text{HCl}$; $\text{CbOCl}_3 \cdot \text{C}_5\text{NH}_5 \cdot \text{HCl}$, and the corresponding bromides; by the second method,



$\text{CbOCl}_3 \cdot \text{C}_5\text{NH}_5 \cdot \text{H}_2\text{O}$; $\text{CbOCl}_3 \cdot 2\text{C}_5\text{NH}_5 \cdot 2\text{HCl} \cdot \text{H}_2\text{O}$. The substances crystallise well, are stable in dry air, and are decomposed by water. The quinoline and pyridine salts are orange-red, the caesium salts brick-red, and the rubidium salts dark red. C. S.

Electrolytic Precipitation of Gold from Cyanide Solutions. BERNHARD NEUMANN (*Zeit. Elektrochem.*, 1906, 12, 569—578).—Dilute solutions of gold in potassium cyanide are electrolysed with lead cathodes and iron anodes. The current efficiency increases during the first few hours and remains almost constant for some time, and finally falls off as the strength of the solution diminishes. With a solution containing 10 grams of gold per cubic metre of 0.05 per cent. cyanide solution, the best efficiency reached varied from 7.5 per cent. with 0.25 ampere per square metre of cathode surface to 0.16 per cent. with 9 amperes per square metre.

Gold may also be deposited on a graphite electrode from a cyanide solution. An attempt to transfer the gold from such an electrode to a copper plate, by using the gilded carbon electrode as anode, in a fairly concentrated solution of potassium cyanide failed. With current densities above 100 amperes per square metre no gold is deposited, whilst with lower currents a very small quantity of loose powder is obtained. By using a solution of gold chloride, preferably containing sodium chloride and hydrochloric acid, at a temperature of 60° to 75° and a current density of 1,000 to 1,500 amperes per square metre, it is, however, possible to strip the gold from the carbon anodes and deposit it on a platinum cathode. The current efficiency varies from 109 to 198 per cent. of that calculated for tervalent gold. T. E.

Platinum-Silver Alloys. JOHN F. THOMPSON and EDMUND H. MILLER (*J. Amer. Chem. Soc.*, 1906, 28, 1115—1132).—These experiments were undertaken with the object of studying the solubility in nitric acid of platinum when alloyed with silver. Alloys containing between 10 and 60 per cent. of platinum were prepared. The method employed for their analysis was based on parting with concentrated sulphuric acid and correcting for the undissolved silver remaining with the platinum. The electrical resistances of the alloys expressed in ohms per sq. mm. per metre were as follows: Alloy containing 10.39 per cent. Pt, 0.0918; 20.59 per cent., 0.1814; 31.46 per cent., 0.2914; 37.89 per cent., 0.3110. The following are the sp. grs. of

the alloys compared with water at 4°: alloy containing 10·39 per cent. Pt, 11·17; 20·59 per cent., 11·80; 31·46 per cent., 12·57; 37·89 per cent., 13·19; 57·05 per cent., 14·25.

On microscopical examination, the alloy containing 10·39 per cent. of platinum was found to consist of crystals set in a non-composite ground mass. On cooling from 1200°, a development of heat was observed at 1045—1050°, and a much larger development at 1000°. The alloy containing 20·59 per cent. Pt, when cooled from 1100°, developed heat at 1085° and possibly also at 995°. The micro-structure showed large, white dendrites in a non-composite ground mass. The alloy containing 31·46 per cent. Pt, on cooling from 1300°, gave marked but irregular developments of heat between 1170° and 1100°. The structure consisted of grey crystals in a dark ground mass. The alloy containing 37·89 per cent. Pt resembled the 31·46 per cent. alloy in structure, but gave sharp developments of heat at 1240° and 1170°. The alloy containing 57·05 per cent. Pt also resembled the 31·46 per cent. alloy in structure; on cooling from 1400°, it gave developments of heat at 1240°, 1180°, and 1090°.

Alloys containing more than 30 per cent. of platinum are much harder than those of a lower platinum content, and the hardness increases rapidly with increase of platinum.

A large number of determinations were made of the solubility in nitric acid of sp. gr. 1·1 and also 1·40 of the foregoing alloys, and also of alloys containing from 0·5 to 25 per cent. of platinum. The results obtained were irregular, and showed clearly that platinum cannot be separated by means of nitric acid from gold, iridium, &c., when alloyed with silver, and proved that assay methods based on this supposed separation are impracticable. The irregularity of the results is considered to be due probably to the existence of platinum-silver compounds.

E. G.

Mineralogical Chemistry.

Metalliferous Veins of the Val de Villé, Vosges, Alsace.
UNGEMACH (*Bull. Soc. franç. Min.*, 1906, 29, 194—282).—A brief account of the character and history of exploitation of the several veins is followed by a detailed description of the thirty-four mineral species found in them. The descriptions are mainly crystallographical; the following analyses are given:

Tetrahedrite from the Sylvester mine is represented by two varieties, which differ in chemical and physical characters. An arsenical variety (anal. I) occurs as rather large crystals, sometimes measuring 5 cm. along the edge, with the tetrahedron as the predominating form and {310} frequently present; the streak is black and the hardness $3\frac{1}{2}$; and the associated minerals are calcite and quartz. An argentiferous variety (anal. II) occurs only as small crystals in which striated faces

of several triakistetrahedra predominate, and {310} is very rarely present; the streak is brownish-black and the hardness is rather less than that of the arsenical variety; the associated minerals are siderite, dolomite, brown-spar, chalcopyrite, galena, blende, quartz, and calcite. The arsenical variety appears to be found only in the upper portions of the veins, giving place in depth to the argentiferous variety. Microscopical examination of polished surfaces, after treatment with acid, shows that the crystals are not homogeneous; particles of native bismuth are enclosed in the tetrahedrite, and it is probable that the presence of zinc is due to the mechanical admixture of blende. The two analyses give the ratios $R''S:Q_2'''S_3 = 3.73:1$ and $3.86:1$ respectively; or, deducting zinc, $3.07:1$ and $3.21:1$ (compare Abstr., 1900, ii, 21).

	Cu.	Ag.	Pb.	Fe.	Zn.	As.	Sb.	Bi.	S.	Total.	Sp. gr.
I.	38.15	trace	0.53	3.77	5.05	6.75	17.47	1.63	25.58	98.93	4.82
II.	34.15	5.94	—	3.79	4.86	1.21	25.24	—	25.22	100.41	5.10
III.	—	—	—	12.72	—	trace	54.06	—	28.02	100.09*	—

* Including SiO_2 , 5.29.

Berthierite from Charbes, forming fibro-lamellar masses and enclosing small grains of quartz, gave anal. III, which agrees with the formula FeS, Sb_2S_3 . Sp. gr. 4.21—4.23.

Botryogen occurs as minute, acicular, brown crystals lining crevices in schists containing pyrites, to the alteration of which it owes its origin. Sp. gr. 1.9—2.2. Analysis IV corresponds with $3MgO, 4Fe_2O_3, 8SO_3, 34H_2O$; or, assuming part of the iron to have originally been ferrous, $(Mg, Fe)O, (Fe, Al)_2O_3, 2SO_3, 9H_2O$.

	Fe_2O_3 .	Al_2O_3 .	MgO .	SO_3 .	P_2O_5 .	H_2O .	Total.
IV.	26.64	2.73	6.18	32.42	0.11	31.04	99.12

The rhombohedral carbonates associated with tetrahedrite in the Sylvester mine include, besides calcite, siderite in lenticular rhombohedra (anal. V); dolomite in curved, rose-red crystals (VI); ankerite in large, yellowish-white rhombohedra (VII); brown-spar in curved, light-brown rhombohedra (VIII), intermediate in composition between pistomesite and siderite.

	$FeCO_3$.	$MgCO_3$.	$MnCO_3$.	$CaCO_3$.	Total.
V.	92.22	7.59	trace	—	99.81
VI.	8.37	37.45	nil	53.12	98.94
VII.	21.85	25.47	—	52.65	99.97
VIII.	61.25	35.08	—	3.10	99.43

L. J. S.

Galena formed during the last Eruption of Vesuvius, April, 1906. FERRUCCIO ZAMBONINI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 235—238).—Crystals of galena were deposited by sublimation on the scoria at the edge of the crater formed as a result of the eruption of Vesuvius in April, 1906. The crystals, which have a maximum breadth of 2 mm., consist, in some cases, of isolated cubes, but are more often grouped either irregularly or in parallel formations. In all probability, this galena owes its formation to the action of hydrogen

sulphide on the vapours of lead chloride according to the reversible reaction: $\text{PbCl}_2 + \text{H}_2\text{S} \rightleftharpoons \text{PbS} + 2\text{HCl}$, a change analogous to that occurring in the reaction of water vapour with ferric or cupric chloride, which determines the formation of hæmatite or tenorite.

T. H. P.

Analysis of Dognacskaite. FRANZ NEUGEBAUER (*Tsch. Min. Mitt.*, 1905, 24, 323—326).—The following analysis of dognacskaite agrees with that originally made in 1884 by Maderspach: S, 17·91; Bi, 71·88; Cu, 10·04 = 99·83. The mineral has a perfect cleavage in one direction, and also a second, less distinct cleavage. Sp. gr. 6·79. The mineral cannot therefore be identical with wittichenite, as suggested by A. Otto (*Abstr.*, 1905, ii, 464), and it appears to be a distinct species with the formula $\text{Bi}_4\text{Cu}_2\text{S}_7$ or $2\text{Bi}_2\text{S}_3 \cdot \text{Cu}_2\text{S}$. The slight excess of bismuth over that required by the formula (70·5 per cent.) is explained by the presence of bismuth-ochre lining small cavities, which probably also affects the sp. gr. quoted above.

L. J. S.

“Phosphate Favas” from the Diamantiferous Sands of Brazil. EUGEN HUSSAK (*Tsch. Min. Mitt.*, 1906, 25, 335—344).—The white to brown rounded or bean-shaped pebbles (called “favas” by the diamond-washers and considered to be a good indication of the presence of diamond) found in the diamantiferous alluvial gravels at several localities in Brazil, particularly in the neighbourhood of Diamantina in Minas Geraes, include several mineral species. Titanium oxide and zirconium oxide favas have been distinguished previously (*Abstr.*, 1899, ii, 432); the following are now described.

(1) *Barium Aluminium Phosphate*.—These favas are usually light to dark brown in colour, but sometimes white; on a fresh fracture they show a compact, jaspéry, microcrystalline structure. Small, rounded grains of quartz and a reddish-brown, powdery material are present as enclosures. Under the microscope, the material is seen to consist of an aggregate of minute granules with feeble refraction and birefringence, and to be optically uniaxial and positive. The sp. gr. varies with the colour from 3·095 to 3·123; the hardness is nearly 6. Analyses I and II, by G. Florence, give, after deducting SiO_2 , Fe_2O_3 and TiO_2 present as enclosed impurities, the formula $\text{BaO} \cdot 2\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$, the barium being partly replaced by calcium and cerium, and also sometimes by strontium. This represents a new mineral, and is named *gorceixite*.

(2) *Strontium Aluminium Sulphato-phosphate*.—This is usually flesh-red, rarely yellow or white, and translucent. It consists of a compact, microcrystalline aggregate of colourless grains and six-sided crystals, which are optically uniaxial and positive, and probably therefore rhombohedral. Sp. gr. 3·21; the hardness is rather lower than that of the barium favas. Analysis III of this shows it to be near, though different from, *svanbergite*: the formula is $\text{SrO} \cdot 2\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot \text{SO}_3 \cdot 5\text{H}_2\text{O}$, and the name *harttite* is proposed.

(3) *Lead Aluminium Phosphate*.—This is white to pale yellow, and has a distinct fibrous structure. Fresh pieces, which have not been water-worn, indicate that the mineral formed a shelly, concentric encrustation. Thin flakes are translucent, and are optically uniaxial

and positive. Sp. gr. 3·626. Analyses IV—VI give the formula $2\text{PbO}, 3\text{Al}_2\text{O}_3, 2\text{P}_2\text{O}_5, 10\text{H}_2\text{O}$, and the mineral may be identified with plumbogummite.

	Al_2O_3 .	Fe_2O_3 .	CeO .	BaO .	SrO .	CaO .	PbO .	P_2O_5 .
I.	35·00	4·10	1·55	15·42	—	3·55	—	22·74
II.	35·20	1·67	2·35	15·30	—	2·24	—	21·47
III.	33·66	—	1·02	—	16·80	2·80	—	21·17
IV.	24·92	—	0·16	—	—	0·62	35·50	22·50
V.	25·31	—	—	—	—	—	35·83	22·11
VI.	25·11	—	36·44					22·30

	SO_3 .	SiO_2 .	TiO_2 .	H_2O .	Total.	Sp. gr.
I.	—	1·55	0·67	14·62	99·20	3·101
II.	—	6·50	0·75	14·73	100·21	3·098
III.	11·53	—	1·42	12·53	100·27	3·21
IV.	—	0·70	—	16·30	100·64	—
V.	—	0·64	—	16·08	99·97	—
VI.	—	—	—	16·19	100·04	—

These minerals belong to the rhombohedral hamlinite group (Abstr., 1900, ii, 602; 1903, ii, 377), which includes the following species:

Florencite	$2\text{CeO}, 3\text{Al}_2\text{O}_3, 2\text{P}_2\text{O}_5, 6\text{H}_2\text{O}$.
Hamlinite	$2\text{SrO}, 3\text{Al}_2\text{O}_3, 2\text{P}_2\text{O}_5, 7\text{H}_2\text{O}$.
Harttite	$\text{SrO}, 2\text{Al}_2\text{O}_3, 2\text{P}_2\text{O}_5, \text{SO}_3, 5\text{H}_2\text{O}$.
Svanbergite	$2\text{SrO}, 3\text{Al}_2\text{O}_3, \text{P}_2\text{O}_5, 2\text{SO}_3, 6\text{H}_2\text{O}$.
Gorceixite	$\text{BaO}, 2\text{Al}_2\text{O}_3, \text{P}_2\text{O}_5, 5\text{H}_2\text{O}$.
Plumbogummite	$2\text{PbO}, 3\text{Al}_2\text{O}_3, 2\text{P}_2\text{O}_5, 7(\text{or } 10)\text{H}_2\text{O}$.
Beudantite	$2\text{PbO}, 3\text{Fe}_2\text{O}_3, \text{P}_2\text{O}_5, 2\text{SO}_3, 6\text{H}_2\text{O}$.
Goyazite	$3\text{CaO}, 5\text{Al}_2\text{O}_3, \text{P}_2\text{O}_5, 9\text{H}_2\text{O}$.

L. J. S.

Petterdite and Datolite. CHARLES ANDERSON (*Rec. Australian Mus.*, 1906, 6, 133—144).—"Petterdite" has recently (Abstr., 1904, ii, 48) been described as a lead oxychloride occurring as white, hexagonal plates at Zeehan, Tasmania. A re-examination of the original material proves it to be identical, crystallographically and chemically, with mimetite. In the original analysis the numbers for arsenic pentoxide and chlorine must have been accidentally interchanged; a new analysis gave:

PbO .	As_2O_5 .	P_2O_5 .	Cl .	Total.
77·14	17·95	2·50	2·46	100·05

Datolite occurring as large brilliant crystals with axinite, calcite, &c., at Dundas, Tasmania, gave the following results on analysis:

SiO_2 .	$\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3$.	CaO .	B_2O_3 .	H_2O .	Total.
36·28	0·95	35·21	20·48	6·48	99·40

The paper contains a crystallographic description of this datolite, and also of crocoite from Tasmania and of axinite from various Australian localities.

L. J. S.

Sodium Sulphate in Secondary Fumaroles of Mt. Pelée. ALFRED LACROIX (*Bull. Soc. franç. Min.*, 1905, 28, 60—68).—The extensive deposits of volcanic ash accumulated by the hot blasts of Mt. Pelée retained, in certain circumstances, their heat for a considerable time, and after tropical rains gave rise to clouds of aqueous vapour. In this way secondary fumaroles were formed, which were quite different from the ordinary type of volcanic fumaroles, and in no way connected with them. Fumaroles of this kind with a temperature of 100° emitted water vapour with a little hydrogen sulphide; those at 400° deposited sal-ammoniac; and those with a temperature of 500—600° gave rise to a transparent, glassy, white to green material, which, on analysis by H. Arsandaux, gave:

SO ₃ .	Na ₂ O.	K ₂ O.	MgO.	CaO.	Al ₂ O ₃ .	NaCl.	Total.
57·1	26·6	6·7	4·4	1·9	1·9	1·4	100 0

The material therefore probably consists of a mixture of thenardite, Na₂SO₄, 46·1; apthitalite, (K,Na)₂SO₄, 22·5; glauberite, Na₂Ca(SO₄)₂, 9·4; magnesium sulphate, 13·2; alumian, Al₂S₂O₆, 5·1; and sodium chloride, 1·4 per cent. Optical examination of the fresh material suggested the presence of polymorphic forms of sodium sulphate, which, on the cooling of the material, became transformed to the more stable thenardite. The sodium sulphate was probably formed by the action of sodium chloride on calcium sulphate in the presence of water vapour at a high temperature; the hydrogen chloride so formed would give rise to ferric chloride and afterwards hæmatite, small crystals of which were observed with the material. L. J. S.

Isomorphism of Northupite and Tychite. AUGUSTE DE SCHULTEN (*Compt. rend.*, 1906, 143, 403—404).—The author has previously prepared northupite artificially (Abstr., 1896, ii, 610; 1897, ii, 146) from a solution containing magnesium chloride and sodium carbonate and chloride, and Penfield and Jamieson have similarly prepared artificial tychite by substituting the corresponding sulphates for the chlorides in the above mixture (Abstr., 1905, ii, 723).

When a solution of magnesium sulphate is added to a solution containing sodium carbonate, chloride and sulphate, a white, amorphous precipitate is formed which is converted into octahedral crystals by prolonged heating on the water-bath; these crystals are homogeneous, and consist of almost pure tychite or northupite, or isomorphous mixtures of the two, according to the relative proportions of sodium sulphate and chloride in the original solution; the results are embodied in the following table:

Quantities employed of		Percentage composition of octahedra	
Na ₂ Cl ₂ .	Na ₂ SO ₄ .	Tychite.	Northupite.
0·68 mol.	0·72 mol.	99	1
0·77 "	0·61 "	76	24
0·79 "	0·59 "	64	36
0·81 "	0·57 "	28	71
0·94 "	0·41 "	6	94

and show that northupite and tychite are isomorphous, and that tychite is the more stable of the two.

The crystals containing 76 per cent. of tychite and 24 per cent. of northupite have a sp. gr. 2.57. M. A. W.

Acid and Alkaline Reaction of Minerals, especially Silicates. FELIX CORNU (*Tsch. Min. Mitt.*, 1906, 25, 417—433).—Experiments were made on the same lines as those made by Kenngott in 1867, but many more mineral species were examined. The finely-powdered mineral is moistened with distilled water, and litmus paper, tincture of litmus, or phenolphthalein used as an indicator. Some minerals give an immediate reaction, whilst others require several hours. All the minerals of the clay and pyrophyllite groups were found to give an acid reaction: nontronite, for example, being strongly acid, whilst pyrophyllite is only feebly acid. Apophyllite is strongly, and calcite feebly, alkaline. The only minerals of those examined which gave no reaction were chalcedony and ilvaite (compare Abstr., 1900, ii, 109; 1902, ii, 112). L. J. S.

Ratio of Iron and Magnesium in Olivine and Rhombic Pyroxene. JOSEF SCHILLER (*Tsch. Min. Mitt.*, 1905, 24, 309—320).—Olivine bombs in the basalt-tuff of the Kapfenstein at Gleichenberg, Styria, consist of large grains of wine-yellow olivine, with dark oil-green bronzite and an emerald-green diopside. The olivine has an optic axial angle $2V = 89^{\circ}55'$, and gave anal. I., corresponding with: Mg_2SiO_4 , 90.2; Fe_2SiO_4 , 9.8 per cent. The bronzite has $2V = 83^{\circ}34'$, and gave anal. II. (by Grete Becke), corresponding with: $\text{Mg}_2\text{Si}_2\text{O}_6$, 86; $\text{MgAl}_2\text{SiO}_6$, 3.9; $\text{MgFe}_2\text{SiO}_6$, 3.2; $\text{Fe}_2\text{Si}_2\text{O}_6$, 6.9 per cent.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	H_2O	Total
I.	40.77	—	1.03	—	9.25	—	48.56	—	—	99.61
II.	54.39	0.12	1.89	2.49	4.52	0.21	34.88	0.05	1.71	100.26

Iron and magnesium are thus in the atomic ratio of about 1:9 in each of these minerals. Several other cases were examined in which olivine and rhombic pyroxene occur together in the same rock, and this ratio (calculated directly from published analyses or indirectly from the optic axial angles) was found to be much the same, but in rocks which contain felspar in addition to olivine and enstatite, the olivine is relatively richer in magnesium than the rhombic pyroxene.

L. J. S.

Lime-silica Series of Minerals. ARTHUR L. DAY and ERNEST S. SHEPHERD (*J. Amer. Chem. Soc.*, 1906, 28, 1089—1114).—The work of Boudouard on the constitution of the lime-silica minerals (*J. Iron and Steel Inst.*, 1905, 339) is criticised, and it is stated that the method employed was not suitable for accurate determinations. It is shown that tricalcium silicate does not exist, and that the only definite compounds formed by the fusion of mixtures of pure lime and silica are the metasilicate and the orthosilicate.

The pseudo-hexagonal metasilicate (Allen, White, and Wright, this vol., ii, 683) melts at 1512° , undergoes inversion into wollastonite at

about 1200° , and has the power of holding small quantities of lime or silica in solid solution.

The orthosilicate melts at 2080° and is capable of existing in three polymorphic forms. The α -form crystallises in the monoclinic system, has a sp. gr. 3.27 and a hardness 5—6 (Mohr's scale). The β -modification forms orthorhombic crystals and has a sp. gr. 3.28. The γ -modification forms monoclinic crystals and has a sp. gr. 2.97 at 25° . The inversion of the α - to the β -form occurs at 1410° , and that of the β - to the γ -form at 675° . The series contains three eutectic points: tridymite and the metasilicate at 37 per cent. CaO, 1417° ; the metasilicate and orthosilicate at 54 per cent. CaO, 1430° ; and the orthosilicate and calcium oxide at 67.5 per cent. CaO, 2015° . The orthosilicate is readily attacked by water. It is found that neither the âkermanite analogue, $4\text{CaO}, 3\text{SiO}_2$, nor the tricalcium silicate, $3\text{CaO}, \text{SiO}_2$, can exist in the two-component system.

During the course of the investigation, determinations were made of some physical properties of calcium oxide and silica. Fused calcium oxide has a sp. gr. 3.32 at 25° and a hardness 3—4; it crystallises in the isometric system, and does not occur in polymorphic forms. Silica does not give a sharp melting point, but begins to melt at about 1600° . When heated above 1000° , pure quartz changes into tridymite, which is the stable crystalline form of silica at temperatures above 1000° . In presence of fused chlorides, quartz glass crystallises as quartz below 760° , and as tridymite above 800° ; crystalline quartz changes to tridymite above 800° , and tridymite to quartz at 750° . The inversion temperature is therefore about 800° , and the change is enantiotropic. Tridymite has a sp. gr. 2.318, and quartz glass a sp. gr. 2.213 at 25° ; the pure natural quartz used had a sp. gr. 2.654, and the artificial crystals a sp. gr. 2.650 at 25° . E. G.

Metasilicates and Trisilicates. GUSTAV TSCHERMAK (*Chem. Centr.*, 1906, ii, 552; from *Sitzungsber. Akad. Wiss. Wien.*, 1906, 115, Abt. I, 217—240).—A continuation of earlier work (Abstr., 1905, ii, 816; *Ann. Rep.*, 1905, 2, 273) on the isolation of silicic acids by the decomposition of natural silicates. The drying curves of the products show a break, one part of the curve corresponding with the drying and the other with the decomposition of the silicic acid. By repeating the weighings twice a day, the positions of the breaks in the curves, and thus the compositions of the silicic acids, have been more accurately determined.

The following orthosilicates were examined. Willemite, Zn_2SiO_4 , the silicic acid from which is coloured blackish-blue by methylene-blue, and, at the break in the curve, contains 36.91 per cent. H_2O (calc. for H_4SiO_4 , 37.37). Monticellite, CaMgSiO_4 , yielded the same acid with 37.91 per cent. H_2O .

Metasilicates, when decomposed by fairly strong hydrochloric acid, yield a product which is flocculent below and gelatinous above; the latter becomes flocculent on addition of water. Under the microscope the outlines of the fragments of the original silicate may be occasionally distinguished. The break in the curve for this product corresponds with the composition H_2SiO_3 , with 22.98 per cent. H_2O . The dry, powdery material, with sp. gr. 1.797, is coloured a deep Prussian-

blue by methylene-blue. Olivine, Mg_2SiO_4 , is remarkable in behaving as a metasilicate, yielding an acid with 22.19—23.79 per cent. H_2O . In dry air the product still continues to lose water, and after a year over calcium chloride the loss on ignition was only 7.95 per cent. Olivine is therefore considered to contain the bivalent group MgOMg , and the formula is written as MgOMgSiO_3 ; in the crystallised condition it probably has a higher, at least double, molecular weight than corresponds with this formula.

The hexagonal calcium silicate obtained from fusion yields an acid with 22.55 per cent. H_2O , and in the fluid condition the silicate has the formula CaSiO_3 , whilst, when crystallised, the molecular weight is at least three times as great. Minerals of the wollastonite group yield metasilicic acid. Thus, the acid from pectolite, $\text{HNaCa}_2\text{Si}_3\text{O}_9$, contains 22.70 per cent. H_2O , and has sp. gr. 1.810—1.814; this still continues to lose water until, after three months, the weight is constant, then containing 17.44 per cent. H_2O , corresponding with $\text{H}_4\text{Si}_3\text{O}_8$ (calc. 16.59°). The fresh acid, when treated with dilute sodium hydroxide, gives a solution with the proportions $\text{Si}_3:\text{Na}_2$ (with metasilicic acid Si_1Na_1). The "pectolite acid" is therefore written as $\text{H}_6\text{Si}_3\text{O}_9$. Wollastonite, $\text{Ca}_2\text{Si}_2\text{O}_7$, yields the same acid with 22.26 per cent. H_2O , which is also unstable, breaking down to ortho- and meta-silicic acids; after three months at 15° it contains 16.87 per cent. H_2O , corresponding with $\text{H}_4\text{Si}_3\text{O}_8$. Wollastonite is therefore considered to be a calcium salt of "pectolite acid."

"Garnet acid," $\text{H}_4\text{Si}_3\text{O}_8$, sp. gr. 1.910—1.906, is coloured pale to bright blue by methylene-blue. Owing to the difficult decomposition of the mineral at 70°, this acid has not yet been obtained in its original form. Grossular yielded an acid with 17.71 per cent. H_2O , and the formula of the mineral is written as $(\text{CaOAlO})_2\text{CaSi}_3\text{O}_8$. The same acid was yielded by zoisite, epidote, and prehnite, the formulæ of which each contain, like garnet, the group $(\text{CaOAlO})_2\text{Si}_3$; zoisite being $\text{AlOH}(\text{CaOAlO})_2\text{Si}_3\text{O}_8$, epidote a mixture of this with the corresponding iron salt, and prehnite the acid salt $\text{H}_2(\text{CaOAlO})_2\text{Si}_3\text{O}_8$.

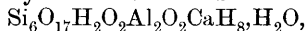
These results suggest that, whilst willemite and monticellite are orthosilicates, olivine and anorthite are metasilicates; that in wollastonite and pectolite the "pectolite acid" is a polymeride of metasilicic acid; that garnet, zoisite, epidote, and prehnite are aluminosalts of "garnet acid." They explain the association of olivine and anorthite, of epidote and prehnite, and the alteration of garnet to epidote.

L. J. S.

Serpentine and Heulandite. SILVIA HILLEBRAND (*Chem. Centr.*, 1906, ii, 553; from *Sitzungsber. Akad. Wiss. Wien.*, 1906, 115, Abt. I, 697—721. Compare preceding abstract).—A compact serpentine yielded on decomposition a silicic acid, the drying curve of which indicated the content of 23.02 per cent. H_2O ; under the microscope, it consists of isotropic splinters with the outlines of the original mineral or of finely granular masses; it has sp. gr. 1.809—1.798, and is coloured a clear Prussian-blue by methylene-blue. This indicates metasilicic acid, and the empirical formula of serpentine suggests the polymeride, $\text{H}_4\text{Si}_2\text{O}_6$ ("serpentine acid"). The voluminous, finely-

flocculent acid yielded by chrysotile contains 27.20—27.80 per cent. H_2O and has sp. gr. 1.725; it is coloured Prussian-blue by methylene-blue, and is distinguished as “chrysotile acid,” $\text{H}_{10}\text{Si}_4\text{O}_{13}$. The formula of chrysotile is written $\text{H}_4(\text{MgOH})_4(\text{MgOMg})\text{Si}_4\text{O}_{13}$. Bowenite yields a powdery acid with 22.64 per cent. H_2O and sp. gr. 1.82; it loses further water until the composition $\text{H}_2\text{Si}_2\text{O}_5$ is reached. Antigorite also yields a powdery acid with 22.79 per cent. H_2O , which is coloured a deep Prussian-blue and is the same as that yielded by compact serpentine. Since serpentine and chrysotile are produced together by the alteration of olivine, it is suggested that the “serpentine acid” has the higher composition $\text{H}_8\text{Si}_4\text{O}_{12}$, and that serpentine, like chrysotile, is $\text{H}_8\text{Mg}_6\text{Si}_4\text{O}_{18}$. This is the first case of isomerism amongst minerals.

Heulandite contains the “heulandite acid,” $\text{H}_{10}\text{Si}_6\text{O}_{17}$, with 19.91 per cent. H_2O (found 20.51 per cent.), which is coloured clear Prussian-blue by methylene-blue. Air-dried heulandite,



loses an appreciable amount of water of crystallisation and of constitution at 90° , and the substance is thereby altered. At 230° , with further loss of water of constitution, the residue has the composition $\text{Si}_6\text{O}_{17}\text{Al}_2\text{O}_2\text{CaH}_6$, and at 400° $\text{Si}_6\text{O}_{17}\text{Al}_2\text{CaH}_2$; above this temperature, the structure of the silicate is destroyed. Since heulandite is decomposed in the presence of a large quantity of water, it follows that the zeolites were not deposited from dilute, but from fairly concentrated solutions.

L. J. S.

A New Mineral of the Zeolite Group. A. PAULY (*Zeit. Kryst. Min.*, 1906, 42, 370—373).—The mineral occurs as minute, colourless, transparent grains, with a vitreous lustre, in a rock composed of quartz, felspar, and sericite, which with sericite-schist forms a zone between granite and dolomite at Hainburg in Lower Austria. It is cubic with a perfect cubical cleavage, and when in crystals appears to have the form of the icositetrahedron $\{211\}$. The hardness is between 3 and 4, and the sp. gr. 2.4—2.5. The mineral is optically isotropic, and has a refractive index of 1.507—1.508. Judging by the amounts of the products obtained on a microchemical analysis, the formula $(\text{Na}_2, \text{Ca})_4\text{Al}_2\text{Si}_5\text{O}_{21}\cdot 6\text{H}_2\text{O}$ is suggested; sulphuric anhydride is also present. Although incompletely determined, the mineral appears to differ from analcite, sodalite, and haüynite.

L. J. S.

A Probably New Zeolite from Elba. GIOVANNI D'ACHIARDI (*Chem. Centr.*, 1906, ii, 453; from *Proc. verb. Soc. Tosc. Sci. Nat.*, 1905, 150—156).—The mineral occurs as groups of small, lustrous, colourless to white crystals in the pegmatite of San Piero in Campo. The crystals have the form of eight-sided pyramids with small basal planes. Sp. gr. 2.165; hardness, 4—4½. Analysis gave:

SiO_2 .	Al_2O_3 .	CaO .	SrO .	MgO .	K_2O .	Na_2O .	H_2O .	Total.
61.41	11.15	5.52	1.14	trace	3.31	2.06	13.51	98.10

corresponding with $3\text{Na}_2\text{O}, 3\text{K}_2\text{O}, 9\text{CaO}, 10\text{Al}_2\text{O}_3, 90\text{SiO}_2, 70\text{H}_2\text{O}$, which is simplified as $(\text{Na}_2, \text{K}_2, \text{Ca})_3\text{Al}_4\text{Si}_{18}\text{O}_{45}\cdot 14(\text{or } 13)\text{H}_2\text{O}$. The composi-

tion is near that of heulandite, but all the other characters suggest a new mineral.

L. J. S.

Mineralogical Notes. JOHN EYERMAN (*Chem. Centr.*, 1906, ii, 453; from *Amer. Geologist*, 1904, 34, 43—48).—The following mineral analyses are given: I, Stilbite, yellow globular aggregates from a quarry on the Delaware river, near Lambertville, New Jersey. II, Natrolite, acicular crystals on calcite, from the same locality. III, Prehnite, massive in thin veins, from the same locality. IV, Orthoclase, milk-white, from Marble Hill, N.J. V, Biotite, silver-white, from Easton, N.J. VI, Biotite, dark-brown, from Easton. VII, Prochlorite, light-green, from William's Bushkill quarry. VIII, Asbestos, from the Delaware river quarry. IX, Serpentine, white and resembling meerschaum, from William's Delaware quarry. X, Meerschaum, from Middletown, Delaware Co., Pennsylvania. XI, Tourmaline, crystals in quartz, from Bushkill Creek, near Easton.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O.	Sp. gr.
I.	58·53	15·84	—	—	8·02	—	0·63	1·65	14·67	2·209
II.	47·80	27·19	—	—	1·50	—	11·62	1·68	9·99	2·228
III.	43·25	20·29	4·87	—	26·76	—	0·59	—	4·38	2·952
IV.	65·73	17·21	2·58	—	2·69	—	2·41	9·59	—	2·609
V.	41·07	23·34	4·35	—	—	23·00	1·60	6·30	0·26	2·712
VI.	40·32	18·03	5·80	—	0·46	24·79	—	10·50	0·25	2·88
VII.	34·01	15·74	—	5·70	0·14	31·20	—	—	12·69	2·533
VIII.	55·25	—	—	2·18	12·66	30·19	—	—	—	—
IX.	44·21	2·72	—	0·52	0·24	40·55	—	—	12·42	2·363
X.	44·58	trace	—	2·13	trace	39·49	—	—	12·91	—
XI.	35·57	24·72	1·17	9·40	3·42	8·29	2·10	0·40	4·23	2·991

	TiO ₂ .	B ₂ O ₃ .	Li ₂ O.	F.
XI. (cont.)	0·18	10·10	trace	not determined

L. J. S.

Asbestiform Mineral from Mexico. JUAN D. VILLARELLO (*Chem. Centr.*, 1906, ii, 452; from *Parergones Inst. Geol. Mexico*, 1904, 1, 133—149).—The mineral is from the Rancho Ahuacatillo in the Zinapécuaro district: it resembles "mountain-cork," and forms soft, flexible lamellæ of a yellowish-white colour, which adhere to the tongue. Sp. gr. 2·18. Analysis gave:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O.	CO ₂ .
52·84	19·02	1·91	4·61	1·56	0·52	0·13	16·75	2·60

Deducting admixed calcite, this corresponds with the formula H₁₀Al₂Si₃O₁₄. The mineral, therefore, belongs to the kaolin group, and approaches montmorillonite.

L. J. S.

Epidote from the Neighbourhood of Chiavriè near Condove in the Valley of Susa. FERRUCCIO ZAMBONINI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 179—183).—Crystals of epidote are described differing in habit from the usual epidotes of Piedmont; several rare forms are present, amongst which may be mentioned {401} and {25·0·12}.

W. A. D.

Zoisite from Lower California. OLIVER C. FARRINGTON (*Field Columbian Museum, Chicago, Geol. Ser.*, 1906, **3**, 55—57).—The mineral is from the Trace mine in the Juarez district, Mexico. It forms divergent, conical groups of long, prismatic crystals, embedded in a matrix of white, granular prehnite. The conical groups are pink on the exterior, passing into colourless and brownish-grey in the centre. Sp. gr. 3.32. Analysis by H. W. Nichols gave :

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	CaO.	MgO.	Na ₂ O, K ₂ O.	H ₂ O.	Total.
38.15	29.50	4.60	0.55	22.71	0.63	traces	3.76	99.90

This gives the formula $H_4Ca_4Al_6Si_6O_{27}$, which differs from that usually accepted for zoisite in containing double the amount of water. This extra water does not, however, appear to be due to any alteration of the mineral, since it is expelled only at a high temperature: over a blast lamp 1.81 per cent. is lost, and in an oven there is a further loss of 1.95 per cent., suggesting that the two molecules of water are differently combined, one with the calcium and the other with the aluminium. The mineral is also unusual in containing a relatively high percentage of iron. L. J. S.

Amphibole from Cevadaes, Portugal. CARL HLAWATSCH (*Festschrift Harry Rosenbusch, Stuttgart*, 1906, 68—76).—The amphibole of the gneissic rocks of this district has been previously described as arfvedsonite and as riebeckite. It has the optic axial plane perpendicular to the plane of symmetry, that is, bisecting the acute angle between the cleavages; the first bisectrix (α) lies near the prism-axis (c); the pleochroism is strong (α , dark steel-blue; β , light brownish-yellow; γ , very dark greyish-green). The prism-cleavage angle is $56^\circ 1'$, and there is a poorer cleavage parallel to the plane of symmetry. Sp. gr. 3.351—3.353. Analysis by M. Dittrich gave :

SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	MgO.	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
49.55	0.34	0.97	16.52	20.38	1.30	0.16	0.90	6.53	0.85	1.85	99.35

This corresponds with 54.7 per cent. $(Na,K)_2(Fe,Al)_2Si_4O_{12}$ + 39.0 per cent. $(Fe,Mn,Mg,Ca)_4Si_4O_{12}$ + 6.3 per cent. H_2SiO_3 .

The mineral is, therefore, intermediate between riebeckite and arfvedsonite; and for amphiboles with the optical orientation given above, the name *osannite* is proposed. The optical characters of the amphiboles vary with the ratio of $Al_2O_3 : Fe_2O_3$, and also possibly with the amount of water present. L. J. S.

The South Bend Meteorite. OLIVER C. FARRINGTON (*Field Columbian Mus. Geol. Ser.*, 1906, **3**, 19—23).—This meteorite, weighing $5\frac{1}{2}$ lbs., was found in 1893 near South Bend, in St. Joseph Co., Indiana. It belongs to the pallasite group, consisting of a sponge of nickel-iron and blebs of olivine in the proportion of about four to one (as calculated from the sp. gr., 4.28, of the entire mass). A thin layer of graphite lines the pores, separating the olivine from the

nickel-iron. Schreibersite is also present. Analysis, by H. W. Nichols, of the nickel-iron gave :

Fe.	Ni.	Co.	Cu.	P.	S.	Total.
90·22	9·35	0·26	0·11	0·05	0·0005	100·04

L. J. S.

Physiological Chemistry.

Action of Carbon Dioxide on the Respiration of Fish. WILLIAM A. OSBORNE and EDITH MUNTZ (*Biochem. J.*, 1906, 1, 377—382).—Tensions of carbon dioxide greater than 1·7 per cent. of an atmosphere produce in gold-fish temporary inhibition of respiration, comparable with the closure of the glottis in mammals. Surface breathing can be produced in the gold-fish not only by oxygen deficiency (confirmatory of Duncan and Hoppe-Seyler), but also by carbon dioxide at a tension varying between 3·2 and 4 per cent. of an atmosphere. The sequence of narcotic manifestations in the gold-fish produced by carbon dioxide is: (1) cessation of voluntary movement, except when irritated; (2) loss of head to stream reflex; and (3) loss of equilibration. No action of the gas on the respiratory centres comparable with that present in man could be discovered in the fish.

W. D. H.

Chemical Changes in the Blood after Bleeding. HEINRICH VON HOESSLIN (*Beitr. chem. Physiol. Path.*, 1906, 8, 431—438).—The removal of relatively large amounts of blood at short intervals in rabbits leads in successive bleedings to a fall in the serum of proteid and total nitrogen, and a rise in sodium chloride and in freezing point. In animals with kidney disease there are some differences in detail.

W. D. H.

Rate of Diffusion of the Salts of the Blood into Solutions of non-Electrolytes, and its Bearing on Theories of Heart Rhythm. WILLEY DENIS (*Amer. J. Physiol.*, 1906, 17, 35—41).—The stimulating salts, sodium chloride and potassium chloride, diffuse more rapidly than the depressor salts, namely, the chlorides of calcium and magnesium. It is suggested that the stoppage of the *Limulus* heart ganglia in isotonic solutions of non-electrolytes may be in part due to the relatively greater concentration of calcium and magnesium salts in the cells and intercellular spaces.

W. D. H.

The Nucleo-proteid of Blood-serum. G. LIEBERMEISTER (*Beitr. chem. Physiol. Path.*, 1906, 8, 439—444).—The properties of the nucleo-proteid which others have described as being present in blood-serum were examined in detail. It contains 0·8 per cent. of phosphorus. Its constant presence is apparently related to the formation and disinte-

gration of the corpuscular elements of the blood, especially of the leucocytes. Its possible relationship to caseinogen formation in milk is also mooted.

W. D. H.

The Properties of the Muscular Tissue of the Walls of Blood-vessels, with Special Reference to the Action of Adrenaline. OSKAR B. MEYER (*Zeit. Biol.*, 1906, 48, 352—397).—Much of the paper relates to the methods of stimulating and obtaining records of the contraction of the muscular tissue of blood-vessels. Oxygen increases the tonus of the vessel wall. Adrenaline stimulates the nerve endings, and the doses necessary are very small; it is antagonised by atropine, cocaine, and curare. Adrenaline causes contraction in the vessels of the lungs. A substance resembling adrenaline is found in the blood. The suprarenal gland forms in addition to adrenaline a material which has the opposite action.

W. D. H.

Influence of Neutral Salts on Salivary Digestion. JOHN BIRT PATTEN and PERCY G. STILES (*Amer. J. Physiol.*, 1906, 17, 26—31).—Ptyalin continues work in the presence of many salts in high concentration, even in the presence of saturated solutions of magnesium sulphate and ammonium chloride. In low concentration, salts of magnesium, calcium, and barium accelerate its action, but with high concentration calcium chloride restrains the action, but this is never true for magnesium sulphate. Ammonium salts are less active in checking digestion than those of sodium and potassium, which are about equal in their effects. Potassium chloride retards less than the bromide, and this less than the iodide. The favourable influence of the fluoride was unexpected. Lithium chloride, usually regarded as the most harmless of foreign substances to living tissues, causes in moderate doses complete inhibition of the enzyme.

W. D. H.

Free Hydrochloric Acid in the Gastric Juice. HEINRICH DRESER (*Beitr. chem. Physiol. Path.*, 1906, 8, 285—301).—Solutions of gastric juice and of dilute hydrochloric acid have been prepared possessing the same concentration as determined by their reaction towards Congo-test paper. The solvent action (that is, the hydrogen ion concentration) of the two solutions on barium chromate and barium oxalate was examined, and it has been found that the gastric juice solution can never dissolve more than 80—98 per cent. of the amount of barium salt dissolved by the hydrochloric acid solution, the usual amount being from 70 to 80 per cent. The filtrations were all made at constant temperature, as slight alterations in temperature affect the results enormously. This point is discussed in detail.

The effect on its peptic action produced by adding varying amounts of glycine to gastric juices appears to be very small, but the effect of altering the amount of hydrochloric acid is marked.

The solvent action of mixtures of hydrochloric acid of known strength with varying amounts of glycine on barium chromate and oxalate has been studied. The amount dissolved in both cases decreases with the

amount of glycine added in a geometrical progression. The electrical conductivities of similar mixtures have been measured. J. J. S.

Digestion in Animals. IV. Fate of Calomel given by the Mouth. M. H. NEMSER (*Zeit. physiol. Chem.*, 1906, 48, 562—570).—Calomel is hardly soluble at all in the gastric contents; it dissolves well in the duodenum, but most of all in the ileum. In the large intestine, it has either all been absorbed or has been precipitated by hydrogen sulphide, so that the faeces contain no mercury in solution. *In vitro*, gastric juice and bile do not dissolve calomel; pancreatic juice dissolves most, then intestinal juice. An alkaline reaction of the food does not hinder solution. The absorption of the mercury of calomel does not begin earlier than the ileum, and is probably completed in the upper part of the large intestine. A considerable portion of the mercury is retained by liver, kidneys, and large intestine for a long time; it apparently acts as a stimulus to these organs. W. D. H.

Action of Chalybeate Waters on Metabolic Processes. VANDEWEYER and WYBAUW (*Chem. Centr.*, 1906, ii, 694; *from Münch. med. Woch.*, 53, 1152—1153).—By the use of chalybeate waters there is an increase in the amount of nitrogen and of sugars absorbed by the system and a decrease in the amount of fat. A perceptible increase in the decomposition of proteid is also observable. In proportion to the total amount of nitrogen, the quantity of uric acid separated is diminished. H. M. D.

Influence of Subcutaneous Injections of Dextrose on Nitrogenous Metabolism. FRANK P. UNDERHILL and OLIVER E. CLOSSON (*J. Biol. Chem.*, 1906, 2, 117—126).—The present experiments demonstrate the great power of the animal body to utilise dextrose given subcutaneously. No toxic action, as described by Scott (*Abstr.*, 1902, ii, 337), was found. W. D. H.

The Decomposition of *dl*-Leucyl-glycine and *dl*-Leucyl-glycyl-glycine in the Organism of Rabbits. EMIL ABDERHALDEN and KARL KAUTZSCH (*Zeit. physiol. Chem.*, 1906, 48, 557—561).—If the two racemic peptides mentioned are given to a rabbit by the mouth or subcutaneously, they are burnt almost completely in the body, only traces reappearing in the urine. The power of the rabbit in this direction is, however, not so great as that of the dog, 4—5 grams of the peptide being the limit of the dose it is able to utilise. W. D. H.

Digestion of Proteids in the Dog's Alimentary Canal. EMIL ABDERHALDEN, KARL KAUTZSCH, and E. S. LONDON (*Zeit. physiol. Chem.*, 1906, 48, 549—556).—Natural digestion in which many enzymes are concerned, working in sequence or together, is, obviously, a more complicated process than artificial digestion, in which as a rule the action of individual enzymes is investigated. In the stomach, traces only of amino-acids are discovered; it is in the intestine that

the final cleavage products are formed which probably are absorbed as such. By the examination of dogs with fistulæ in various parts of the alimentary canal, the amount of the amino-acids can be determined, and the rate of absorption judged. In the present experiments the total amino-acids were estimated. Among these glycine, leucine, alanine, tyrosine, aspartic acid and glutamic acids were identified, but not estimated. Absorption is not confined to the upper part of the small intestine.

W. D. H.

The Rate of Proteid Decomposition in Different Diets.

HANS VOGT (*Beitr. chem. Physiol. Path.*, 1906, 8, 409—430).—The urine was examined at frequent intervals during the day, in order to determine the rate at which the nitrogen and phosphoric acid pass into that secretion when different diets are administered. The experiments were made on dogs and men in health and in certain pathological states. The results hitherto obtained are given in tables and curves.

W. D. H.

Ferments concerned in Nuclein-metabolism.

ALFRED SCHITTENHELM (*Zeit. physiol. Chem.*, 1906, 48, 571—573).—Polemical against W. Jones and Austrian (compare this vol., ii, 561).

W. D. H.

Can Nitrogenous Equilibrium in the Animal Organism be Attained by Means of Heteroalbumoses? VALDEMAR HENRIQUES and C. HANSEN (*Zeit. physiol. Chem.*, 1906, 48, 383—386. Compare Pollitzer, *Abstr.*, 1886, 377; Blum, *Abstr.*, 1900, ii, 667).—Feeding experiments made on white rats with heteroalbumose from Witte peptone and also with dysalbumose indicate that both these substances can protect the organism from loss of nitrogen.

J. J. S.

The Action of Lecithin on Animal Metabolism. B. SLOWTZOFF (*Beitr. chem. Physiol. Path.*, 1906, 8, 370—388).—A complete summary of previous work is given. Three experiments on human beings have shown that retention of nitrogen, produced by the action of lecithin on the organism, is accompanied by a diminution of the amount of sulphuric acid in the urine. This indicates that the administration of lecithin causes a retention of proteids. The diminution in nitrogen excreted during the lecithin period is mainly due to a diminution of carbamide in the urine.

The nitrogen increase is accompanied by a retention of phosphoric acid.

J. J. S.

The Digestive Gland in Mollusca and Decapod Crustacea.

HERBERT E. ROAF (*Biochem. J.*, 1906, 1, 390—397).—In crabs, digestion of fibrin proceeded more actively in an alkaline medium. Starch was converted into reducing sugar and sucrose inverted. No hydrolysis of olive oil was observed, but methyl acetate was readily split into methyl alcohol and acetic acid. No evidence of an enterokinase was found. With the molluscs (limpets, &c.) the results were the same except that fibrin digestion proceeded most actively in acid

media. Some details of the chemical composition of the glands themselves are added.

W. D. H.

Urobilin. F. FISCHLER (*Zeit. physiol. Chem.*, 1906, 48, 419—421. Compare this vol., ii, 470).—Further experiments have proved that when the animals with biliary fistulæ are bound in such a way that they cannot lick up bile, then on the administration of amyl alcohol, phosphorus, or tolylenediamine, no urobilin is formed in the bile. The urobilin is only found when the animals have been able for some time to lick up their bile; the contrary results obtained previously were due to insufficient precaution having been taken to prevent this occurring.

J. J. S.

Amylase and Maltase of Pancreatic Juice. H. BIERRY and GIAJA (*Compt. rend.*, 1906, 143, 300—302. Compare Abstr., 1905, ii, 643).—Amylase acts best in very slightly alkaline media. Pancreatic juice, dialysed through collodion in presence of distilled water, loses all power of action on starch and maltose; its properties are, however, restored on adding a suitable electrolyte.

N. H. J. M.

Time Relations of Tryptic Action. SVEN G. HEDIN (*J. Physiol.*, 1906, 34, 370—371).—The digestion time is inversely proportional to the amount of trypsin solution employed. This has been found previously to be valid as far as the splitting off of nitrogen is concerned; it is in the present research confirmed with regard to the splitting off of phosphorus from casein.

W. D. H.

Trypsin and Antitrypsin. SVEN G. HEDIN (*Biochem. J.*, 1906, 1, 474—483).—In these experiments the substrate employed was caseinogen, and the antitrypsin used, that of the blood serum (serum albumin). It was found that the amount of trypsin it neutralises is independent of the dilution. The antitrypsin can be neutralised completely by a sufficient amount of trypsin, but the reverse does not hold good, and the amount of trypsin neutralised is variable. It was impossible to render active again the neutralised trypsin. Antitrypsin is destroyed by 0.1 to 0.2 per cent. of acetic acid at 37° for eight hours.

W. D. H.

Antitryptic Effect of Charcoal. SVEN G. HEDIN (*Biochem. J.*, 1906, 1, 484—495).—Trypsin is neutralised by charcoal in two consecutive stages: (1) it is adsorbed, and completely so if enough charcoal is used; it is, however, readily transferred to added caseinogen; (2) it undergoes fixation, by which it is rendered inaccessible to added caseinogen. The amount fixed is larger, the larger the amount of trypsin, the longer the time of interaction, and the higher the temperature. The action of antitrypsin and charcoal agrees in all respects.

W. D. H.

The Influence of Diffusibility and the Solubility of Lipoids on the Rate of Intestinal Absorption. MARJAM KATZENELLENBOGEN (*Pflüger's Archiv*, 1906, 114, 522—534).—The velocity of absorption is greater, the greater the lipid-solubility of the substance to be absorbed. The part played by the rate of diffusion is illustrated

by experiments on the absorption of alkaline formates, acetates, and valerates. During absorption the intestine performs concentrative work on sodium chloride.

W. D. H.

Monoamino-acids of the Membrane of Hens' Eggs. EMIL ABDERHALDEN and ERICH EBSTEIN (*Zeit. physiol. Chem.*, 1906, **48**, 530—534).—The membrane is composed of the substance called ovo-keratin. It yields on hydrolysis the following percentages of mono-amino-acids: glycine, 3.9; alanine, 3.5; aminovaleric acid, 1.1; leucine, 7.4; proline, 4.0; glutamic acid, 8.1; and aspartic acid, 1.1.

W. D. H.

Monoamino-acids of Keratin from the Eggs of Testudo graeca. EMIL ABDERHALDEN and EDUARD STRAUSS (*Zeit. physiol. Chem.*, 1906, **48**, 535—536).—The egg-shells of tortoise eggs are composed of a substance similar to the ovo-keratin of hens' eggs, but the quantity of material available was insufficient for complete investigation. A few analytical figures are given.

W. D. H.

Proportion of Lecithin in Egg Yolk. ARMAND MANASSE (*Chem. Centr.*, 1906, ii, 805—806; from *Biochem. Zeit.*, **1**, 246—252).—The mean amount of lecithin in the yolk of hen's egg is 9.41 per cent.

H. M. D.

Chemistry of the Placenta. WILHELM CRAMER and JAS. LOCHHEAD (*Proc. Physiol. Soc.*, 1906, xxiv—xxv; *J. Physiol.*, **34**).—In the second half of pregnancy in sheep and rabbits, the nucleo-proteids of the maternal portion of the placenta differ in composition from those obtained from the foetal portion. Glycogen is found mainly or exclusively in the maternal portion. Glycerol extracts do not contain peptic, tryptic, or ereptic ferments. Amylolytic and glycogen-splitting ferments are demonstrable in most cases, but differences in the two animals and at different stages seem to exist.

W. D. H.

Comparison of Muscles, Electrical Organ, and Blood-serum of *Torpedo ocellata*. SILVESTRO BAGLIONI (*Beitr. chem. Physiol. Path.*, 1906, **8**, 456—471).—The chemical composition of the electrical organ of *Torpedo*, although it is so closely related developmentally and morphologically to the muscles, is very different from that of the muscles. This must bear some relation to the different physiological functions the two tissues exhibit. The chemical composition of the electrical organ is more like that of the blood-serum of the same animal, being rich in water and very poor in proteids. Both are rich in alkali salts, especially of sodium, and so again differ from the muscles. The amount of urea is about equal throughout. The amount of glycogen is somewhat less in the electrical organ than in the muscles.

W. D. H.

Muscle Extracts. IV. Occurrence of Carnosine, Carnitine, and Methylguanidine in Flesh. R. KRIMBERG (*Zeit. physiol. Chem.*, 1906, **48**, 412—418. Compare Gulewitsch, *Abstr.*, 1900, **i**, 516, 782; 1905, **i**, 726; this vol., **i**, 637).—The three bases carnosine, carnitine

and methylguanidine are not only present in meat extract, but also in the flesh of freshly killed oxen.

It is suggested that Kutscher's novaine (*Zeit. Nahr. Genussm.*, 1905, 10, 553) is identical with carnitine. J. J. S.

Action of Proteolytic Ferments of the Animal Organism.

EMIL ABDERHALDEN and ANDREW HUNTER (*Zeit. physiol. Chem.*, 1906, 48, 537—545).—The juice expressed from muscles, liver, and kidneys of the rabbit is able to split up the three peptides, *dl*-leucyl-glycine, glycyl-*dl*-alanine, and glycyl-glycine. W. D. H.

Physiology of Mollusca. III. LAFAYETTE B. MENDEL and HAROLD C. BRADLEY (*Amer. J. Physiol.*, 1906, 17, 167—176).—The pedal muscle of *Sycotypus canaliculatus* contains glycogen in abundance, taurine, xanthine, hypoxanthine, and fermentation lactic acid. Glycine was not found. The muscle extractives, therefore, closely resemble those previously described in other molluscs. The blood proteids contain both copper and zinc. Hæmoglobin is present in some of the more active tissues, such as the heart and pharyngeal muscles. W. D. H.

Does the Lung Tissue invert Lactose. MAX RIEHL (*Zeit. Biol.*, 1906, 48, 309—312).—Neither extracts nor the residues after extraction of the lungs of dog, calf, and pig are able to invert lactose. W. D. H.

Crystals in the Nuclei of Liver Cells. PERCY T. HERRING (*Proc. Physiol. Soc.*, 1906, xxi—xxiii; *J. Physiol.*, 34).—Crystals composed of hæmoglobin or possibly methæmoglobin were described by Browicz in the liver cells (nucleus and cytoplasm) of dogs. He believes hæmoglobin enters the cells from the blood stream both in solution and in disintegrating blood corpuscles, but considers crystal formation is post-mortem, due to the action of formaldehyde, which was used as a fixative. The present observations show that these crystals are not at all uncommon; hitherto they have been found only in dogs, and it is not necessary to inject hæmoglobin or hæmolytics into the blood stream to demonstrate them. They look like oxyhæmoglobin crystals, and behave like red blood corpuscles in their reaction to stains. They are seen only in the nuclei, the non-rupture of which is believed to show they are formed ante-mortem. Red corpuscles in all stages of disintegration are found within the liver cells also. W. D. H.

The Post-mortem Flow of Lymph. FRANCIS A. BAINBRIDGE (*J. Physiol.*, 1906, 34, 275—281).—After the injection of dextrose solution or saline solution, the capillary pressure in the liver after death is higher than in the normal animal. The post-mortem flow of lymph which Asher observed after inducing hydræmic plethora is chiefly derived from the liver, and almost disappears after ligation of the portal lymphatics. The small flow which sometimes still remains is derived from the intestines; it is regarded as lymph formed during

life and squeezed into the thoracic duct by post-mortem intestinal movements. There is no post-mortem secretion of bile or pancreatic juice, nor does dextrose increase the tissue-metabolism. The lymph is formed by filtration through the liver capillaries as a result of the increased capillary pressure. The post-mortem flow of lymph after the injection of peptone is due either to increased filtration through abnormally permeable capillaries or to increased metabolism in the liver cells; the former view is regarded as the more probable.

W. D. H.

The "Protagon" of the Kidneys. THEODOR PANZER (*Zeit. physiol. Chem.*, 1906, 48, 519—527).—The material described by Stoerck as protagon in the epithelial cells of certain forms of kidney disease (large white kidney) was separated by the use of boiling acetone; it is doubly refracting, and gives the colour tests for fat. It is, however, not protagon, but an ester of cholesterol with a fatty acid, probably oleic.

W. D. H.

Composition of Bone in Osteomalacia. FRANCIS H. MCCRUDDEN (*Amer. J. Physiol.*, 1906, 17, 32—34).—In osteomalacia, there is an absorption of calcium and phosphorus, and an increase of magnesium salts and of material, probably organic, which is rich in sulphur. The following analyses per cent. are given from the horse:

	Normal bone.	Bone in osteomalacia.
CaO	33 to 35	18—20.
MgO	0·1	0·5
P ₂ O ₅	23	16
S	0·1	0·4

W. D. H.

Formation of Creatinine in the Organism. MAX JAFFÉ (*Zeit. physiol. Chem.*, 1906, 48, 430—468. Compare Czernecki, *Abstr.*, 1905, ii, 467).—Numerous experiments, made by feeding dogs and rabbits with guanidineacetic acid (glycoeyamine), show that the introduction of this substance into the system produces an increase in the amount of creatine contained in both the urine and muscle of the animal. This is due to the methylation of the glycoeyamine. The creatine was estimated by conversion into the zinc chloride compound. This conversion is not theoretical, and under the most favourable conditions gives a 94 per cent. yield only.

Glycoeyamine picrate crystallises in slender, yellow needles melting at 199—200°. Glycoeyamine does not yield an additive compound with zinc chloride. The *hydrochloride* forms large crystals readily soluble in water or alcohol. The acetate crystallises in thin plates almost insoluble in concentrated acetic acid, but is readily hydrolysed by water. The base does not give characteristic reactions with sodium nitroprusside or with sodium picrate and alkali. It may be transformed into glycoeyamidine by prolonged boiling with dilute hydrochloric acid. Glycoeyamidine yields an *additive product* with zinc chloride, (C₃H₅ON₃)₂.ZnCl₂, which crystallises in small, rhombic plates.

Glycocyamidine picrate melts at 210°.

When glycocyamidine is administered subcutaneously to animals, both creatine and glycocyamidine are found in the urine.

Arginine does not appear to be a substance from which creatine can be formed. J. J. S.

The Source of Thiocyanate in the Organism. K. WILLANEN (*Chem. Centr.*, 1906, ii, 619; from *Biochem. Zeit.*, 1, 129—134).—After the introduction of large quantities (5—10 grams) of glycine, creatine, creatinine, or adenine into the stomach of the rabbit, thiocyanate was detected in the urine. These substances, therefore, are the source of the thiocyanate in the organism. H. M. D.

Reactions of Earthworms to Salts. GEORGE H. PARKER and C. R. METCALF (*Amer. J. Physiol.*, 1906, 17, 55—74).—*Allolobophora fatida* withdraws from solutions of chlorides at rates which show these salts to be stimulating in the sequence sodium, ammonium, lithium, and potassium. To man, all four solutions taste saltish with slight differences; the salt taste is due to chlorine; hence in man the anion is the chief stimulus, in the worm, the cation. The gustatory protoplasm of the two organisms must be chemically differentiated in these two directions. If the earth inhabiting *Helodrilus* is used instead of the manure inhabiting *Allolobophora*, the same solutions stimulate in the order potassium, ammonium, sodium, and lithium. The gustatory protoplasm of the worms is therefore adapted to their environment.

W. D. H.

Osmotic Effect of Various Salt Solutions on Cell Volume. HERBERT E. ROAF (*Biochem. J.*, 1906, 1, 383—389).—There is a certain strength of solution in which tadpoles are best suited to maintain an equilibrium between their body fluids and their surrounding medium. A decrease in concentration below this causes an increased loss of weight, which reaches a maximum in distilled water. Increase in the concentration causes a progressive increase in loss of weight, which becomes more marked as the strength at which the organisms are killed is reached. The current view that, when plasmolysis occurs, the solution used is isosmotic with the cell contents, requires revision. It is evident from the tables presented that long before the isosmotic strength is reached there is progressive loss of weight. It is not equality of pressure, but a difference which is maintained by the cell.

W. D. H.

The Use of Soluble Prussian Blue for Investigating the Reducing Power of Animal Bioplasm. DAVID F. HARRIS and WILLIAM MOODIE (*Proc. Physiol. Soc.*, 1906, xxxii—xxxiv; *J. Physiol.*, 34); D. F. HARRIS and JAMES C. IRVINE (*Biochem. J.*, 1906, 1, 355—363).—Potassium ferric ferrocyanide injected into blood vessels *intra vitam* is retained in them *post mortem*; by being transformed into the green or white potassium ferrous ferrocyanide, this demonstrates the biochemical reducing power which the tissues possess. It accounts for the frequent failure, from the histological standpoint, of injecting

Prussian blue with gelatin mass to demonstrate the arrangement of blood vessels; but such preparations may be restored to a vivid blue by irrigation with hydrogen peroxide. The reducing power is very strikingly demonstrated by perfusing the compound through a surviving kidney until a flow from the ureter of the leuco or pale green salt is established.

W. D. H.

Nature of Methylene-Blue-Eosin Staining. J. O. WAKELIN BARRATT (*Biochem. J.*, 1906, i, 406—428).—Staining by methylene-blue-eosin in alcoholic solution is a chemical reaction. Methylene-blue-eosin in alcoholic and aqueous solution exhibits colloidal characters, as do also methylene-blue and eosin in the water-soluble and alcohol-soluble forms. The paper is illustrated by charts of absorption spectra.

W. D. H.

Why does the Urine become Cloudy on Boiling? HANS MALFATTI (*Beitr. chem. Physiol. Path.*, 1906, 8, 472—480).—The relationships of the urinary phosphates to the acidity of the urine, and the changes they undergo when that fluid is boiled, and which frequently lead to a cloudiness appearing there, are discussed.

W. D. H.

The Detection and Physiological Relations of Glyoxylic Acid. ERNST SCHLOSS (*Beitr. chem. Physiol. Path.*, 1906, 8, 445—455).—A modification of Eppinger's test for glyoxylic acid in urine is described, and stated to give trustworthy results. Eppinger stated that the administration of various substances (alcohol, glycine, glycolic acid, sarcosine, betaine) led to the appearance of the acid in the urine. This was not confirmed. A positive result was, however, obtained with allantoin feeding. This is regarded as important, because of Almagia's view of the relationship of glyoxylic acid to uric acid metabolism. From the examination of a number of organs, it is believed that glyoxylic acid is destroyed in the body, especially by the liver.

W. D. H.

Occurrence of Amino-acids in the Urine of Children. HANS RIETSCHEL and LEO LANGSTEIN (*Chem. Centr.*, 1906, ii, 537; from *Biochem. Zeit.*, 1906, 1, 75—80).—No appreciable quantity of amino-acids could be found in the urine of infants. 0.32 gram of leucine was isolated from the urine of a child suffering from croup and pneumonia.

P. H.

Excretion of Optically Active Amino-acids in the Urine. EMIL REISS (*Beitr. chem. Physiol. Path.*, 1906, 8, 332—338).—Various optically active amino-acids were administered to dogs and men *per os*, and the amounts of amino-acids in the urine determined by naphthalenesulphonic chloride.

d-Leucine appears to be completely assimilated by dogs, *l*-tyrosine completely by men and largely by dogs.

d-Alanine is much more readily utilised by the organism than *l*-alanine (compare Plant and Reese, this vol., ii, 110).

J. J. S.

Detection of Toxic Bases in Urine. II. FRIEDRICH KUTSCHER and ALFRED LOHMANN (*Zeit. physiol. Chem.*, 1906, 48, 422—424. Compare this vol., ii, 471).—The precipitate, obtained by the addition of silver nitrate and barium hydroxide after precipitation of alloxuric bases with silver nitrate and nitric acid, contains, in addition to creatinine, a base, probably dimethylguanidine; this may be purified by means of its *picrolonate*, $\text{NH}:\text{C}(\text{NH}_2)\cdot\text{NM}_2\cdot\text{C}_{10}\text{H}_8\text{O}_5\text{N}_4$, which decomposes at 275—278°. The *picrolonate* of Schenck's s-dimethylguanidine melts and decomposes at 260—262°. J. J. S.

Bacterial Processes in Advanced Anæmia. CHRISTIAN A. HERTER (*J. Biol. Chem.*, 1906, 2, 1—70).—The *Bacterium aerogenes capsulatus* frequently occurs in greatly increased quantities in the human intestine, and with this is usually associated a diminution in the number of *B. coli communis* present. The former organism is characterised especially by producing the butyric fermentation, and the large amount of gas so formed leads to flatulence. The symptoms vary with the severity of the infection, and in bad cases, especially in children, anæmia of a severe type supervenes. This is apparently due to the fact that the organism is an active hæmolyising agent, but the hæmolysis it produces *in vitro* is only in part attributable to ammonium butyrate. W. D. H.

Hydrochloric Acid and Cancer. F. W. MORTON PALMER (*Biochem. J.*, 1906, 1, 398—405).—Observations are given confirming previous results that the hydrochloric acid is lessened or absent in most cases of cancer even if the stomach is not involved. Psychical influences like dread of death were excluded, as the diminution was often most marked in cheerful patients, and least marked in the opposite class. Dyspepsia is absent as a rule; this may be explained by supposing that a substitution of intestinal for gastric digestion takes place. W. D. H.

Glycosuria caused by Excess of Carbon Dioxide in the Respired Air. EDWARD S. EDIE (*Biochem. J.*, 1906, 1, 455—473).—The glycosuria in asphyxiation is due to excess of carbon dioxide, not to diminution of oxygen. If 10—15 per cent. of the former gas in air is breathed, even though the oxygen be increased glycosuria sets in. If the oxygen is reduced to less than 6 per cent. without excess of carbon dioxide, it does not. The amount of carbon dioxide mentioned produces anæsthesia in dogs and cats, and in producing glycosuria also acts like other anæsthetics. It is suggested that the glycosuria is produced by the gas uniting with proteid and liberating the carbohydrate previously so combined. W. D. H.

Secretin in Relation to Diabetes Mellitus. FRANCIS A. BAINBRIDGE and ARTHUR P. BEDDARD (*Biochem. J.*, 1906, 1, 429—445).—In three cases of severe diabetes, secretin by the mouth had no effect on the output of sugar: yet it was possible in one case to abolish the glycosuria by dieting after a long latent period. In cases where benefit has been ascribed to the secretin, it might therefore have been

due to the feeding. After death, in only one out of six cases was prosecretin present in normal quantities; but the one case combined with observations on pancreatic diabetes in cats negatives the view that absence of prosecretin is a necessary result in severe diabetes. Three of the remaining five cases died of coma, and the other two of intercurrent disease; in the three coma cases, prosecretin was absent; in the other two it was scanty. Acid intoxication, which precedes coma, may prevent the normal production of prosecretin; if this is the case, its absence has little significance. It is possible, on the other hand, that prosecretin is deficient from the outset, and that this is the actual cause of the diabetes; but here it would be necessary to assume that secretin is the stimulus to the internal as well as to the external secretion of the pancreas, and that the pancreas is normal. In rabbits, artificial acid intoxication does not produce lessening of prosecretin, and an attempt to artificially reduce prosecretin to see whether diabetes follows is being attempted.

W. D. H.

Treatment of Diabetes by Acid Extract of Duodenal Mucous Membrane. BENJAMIN MOORE, EDWARD S. EDIE, and JOHN H. ABRAM (*Biochem. J.*, 1906, 1, 446—454).—In a preliminary paper (this vol., ii, 186) it was stated that administration of acid extract of duodenal mucous membrane was beneficial in diabetes, although caution was exercised in drawing conclusions from so few cases. Since then many more cases have been treated in this way, but in the majority of cases without avail, as in Bainbridge and Beddard's results (see preceding abstract). In a few cases, a decided drop in sugar excretion occurred, and this was not attributable to dieting, since dieting by itself, tried for some time before the secretin was given, did not produce the effect.

W. D. H.

Adrenaline Glycosuria. FRANK P. UNDERHILL and OLIVER E. CLOSSON (*Amer. J. Physiol.*, 1906, 17, 42—54).—Adrenaline given to dogs subcutaneously causes no increase of ammonia or decrease of urea in the urine as Noël Paton stated. The distribution of nitrogen in urea, ammonia, and creatinine is unchanged. The ability of the organism to utilise dextrose is not seriously impaired, and repeated doses fail to produce glycosuria, tolerance being established. Adrenaline glycosuria bears no relation to ordinary diabetes in man, and is essentially of nervous origin. The sympathetic causes either the sugar-storing organs to relinquish their store or prevents the storage of glycogen.

W. D. H.

Treatment of Trypanosomiasis by Benzidine Colours. M. NICOLLE and FELIX MESNIL (*Ann. Inst. Pasteur*, 1906, 20, 417—448).—Ehrlich's statement that the material called trypan-red cures trypanosomiasis led the authors to investigate a large number of other coloured derivatives of benzidine. They find that the disazo-compounds prepared from H acid (8-amino- α -naphthol-3:6-disulphonic acid) with (1) *o*-dichlorobenzidine in alkaline media, (2) with *o*-tolidine in alkaline solution, and (3) with *o*-tolidine first in acid, then in alkaline media, act curatively in the disease Nagana of mice in a single dose.

The product from benzidine and naphthylenediaminedisulphonic acid, 2:7:3:6, is less active, so is trypan-red. The bulk of the paper relates to the chemical structure of the pigments. Later details are promised regarding their action on various diseases caused by trypanosomes.

W. D. H.

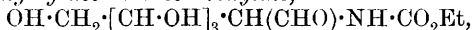
Chemical Constitution and Physiological Action. CHARLES R. MARSHALL (*Proc. Physiol. Soc.*, 1906, xxx—xxxii; *J. Physiol.*, 34).—*Organic Nitrates*.—All the nitrates of polyhydric alcohols and sugars dilate blood-vessels. The presence of a carboxyl group inhibits this effect. The presence of a hydroxyl group in a polyatomic nitrate diminishes the vaso-dilating action.

Synthetic Tropeines.—The addition of a molecular quantity of an alkali hydroxide renders pilocarpine inactive. The same is true for two tropeines prepared synthetically by Jowett (*Trans.*, 1906, 89, 357), namely, terebyltropeine and phthalidecarboxyltropeine, both of which have an atropine-like effect.

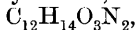
Strychnine Derivatives.—Amino-, nitro- or bromo-strychnine acts like strychnine, but more feebly. Dibromostychnine produces paralysis in frogs before its strychnine action, and as a convulsant is weaker than the others.

Silver Compounds.—Experiments by Krönig and Paul seemed to prove that the bactericidal power of salts is due to the ions into which they dissociate in solution, and in the case of silver compounds the effect was attributed to free silver ions. This is not true for ammoniacal silver chloride solutions, nor for certain other therapeutic compounds of silver. Possibly these undergo an intracellular change, as some double compounds of silver which give no free silver ions on solution are not bactericidal even in concentrated solution. W. D. H.

Ethyl Glucosaminocarboxylate and its Behaviour in the System of a Dog suffering from Pancreas-diabetes. J. FORSCHBACH (*Beitr. chem. Physiol. Path.*, 1906, 8, 313—325).—A résumé of previous work on the effects of glucosamine on the organism is given. *Ethyl glucosaminocarboxylate*,



is readily prepared by the gradual addition of ethyl chlorocarbonate to a cold mixture of glucosamine hydrochloride with an excess of pure lead oxide. It crystallises from dilute alcohol in minute, colourless crystals, melts at 166—167° after turning brown at 165°, and has $[\alpha]_D + 33.18^\circ$. One hundred c.c. of a cold saturated aqueous solution contain 32.66 grams, and 100 c.c. of a cold saturated alcoholic solution 0.2675 gram of the ester. It is insoluble in ether or benzene, gives Moli's furfuraldehyde reaction, but not Ehrlich's *p*-dimethylaminobenzaldehyde reaction. It reduces bismuth and cupric salts, but is not fermentable. With phenylhydrazine, it yields a product,



melting at 180—181°. This is probably formed by the elimination of a molecule of water and one of ethyl carbamate from the phenylhydrazone of the ester.

Experiments have shown that the ethyl ester is oxidised in the animal body even in the case of pancreas-diabetic dogs, and is not utilised in the formation of sugar. J. J. S.

Physiological Action of Phytin Acid. LAFAYETTE B. MENDEL and FRANK P. UNDERHILL (*Amer. J. Physiol.*, 1906, 17, 75—88).—A solution of anhydro-oxymethylene-diphosphoric acid, the acid radicle of phytin prepared from wheat bran, is quite stable. In sufficient concentration it inhibits bacterial growth, but its salts are not noticeably bactericidal. No evil results follow the administration of the sodium salt by the mouth or by various kinds of injection. The free acid is more toxic. Purgation is not a constant result. There is no effect on nitrogenous metabolism; the phosphorus is eliminated as inorganic phosphates, mainly by the kidneys. W. D. H.

Physiological Action of Tutin. CHARLES R. MARSHALL (*Proc. physiol. Soc.*, 1906, xxix—xxx; *J. Physiol.*, 34).—Tutin is a crystalline glucoside existing in three species of *Coriaria* indigenous to New Zealand. This plant has proved a serious hindrance to the raising of cattle in that colony. All domestic animals are affected in the same way. The heart-rate drops, the temperature falls, breathing is quicker, and the animal dies either in convulsions or from exhaustion. 0.0025 gram per kilo. of body-weight is the lethal dose in rabbits, administered hypodermically. Spasms are obtained so long as the bulb remains intact, but are better marked if a portion of the corpora quadrigemina is left also. They are not produced below a section of the spinal cord. W. D. H.

Colloidal Compound of Strychnine. ORVILLE H. BROWN (*J. Biol. Chem.*, 1906, 2, 149—157).—A full account of the pharmacological action of this compound, a preliminary report of which has already appeared (this vol., ii, 188). W. D. H.

Relation between Proteids and Electrolytes. IV. Ion-concentration and Ion-toxicity in Systems of Proteids, Metallic Salts, and Water. S. LA FRANCA (*Zeit. physiol. Chem.*, 1906, 48, 481—488).—The presence of proteid diminishes the electrical dissociation of different metallic salts (such as copper sulphate, mercuric nitrate, and silver nitrate), so that the number of metal ions in solution is extraordinarily small. The parallelism between the toxicity of these solutions and the number of metal ions leads to the conclusion that the metals are only poisonous when in an ionic condition. W. D. H.

Inhibition of the Toxic Influence of Solanine by Carbon Dioxide. WALTER HAUSMANN and O. WOZASEK (*Chem. Centr.*, 1906, ii, 682; from *Centr. Physiol.*, 20, 304—309).—The hæmolytic action of solanine is inhibited by carbon dioxide. If the carbon dioxide is removed from solution by a current of air, the hæmolytic activity is restored. The hæmolytic action occurs in an oxygen-free atmosphere,

and the inhibitive influence of carbon dioxide cannot be attributed to lack of free oxygen. The action of sapotoxine is not affected by carbon dioxide.

H. M. D.

Chemistry of Vegetable Physiology and Agriculture.

Formation of Acid and Alkali in Artificial Culture Media of Moulds. EDUARD KOHN and FRIEDRICH CZAPEK (*Beitr. chem. Physiol. Path.*, 1906, 8, 302—312).—Artificial culture media containing ammonium chloride will only allow of the growth of cultures of *Aspergillus niger* when neutral or only faintly acid. During the growth of the organism, the medium becomes more strongly acid owing to the withdrawal of ammonia, and this ultimately interferes with the growth of the mould. The same phenomena are met with in the case of ammonium sulphate, but to a less extent, and with ammonium phosphate to an even smaller extent. The inhibiting effects of ammonium bromide, iodide, and fluoride are, to a large extent, due to the formation of free acid, and can be largely avoided by keeping the solutions neutral. Ammonium chlorate and iodate act as poisons, but their activity is also due to the secondary formation of acid.

Penicillium glaucum is somewhat more resistant to dilute acid than *Aspergillus*.

The formation of free alkali in the culture medium occurs in the case of denitrifying organisms, also during the growth of moulds in solutions containing ammonium acetate or propionate, methylamine acetate, &c.

A mixture of ammonium chloride and acetate in the medium permits of vigorous growth, as the acidity caused by the one salt counterbalances the alkalinity produced by the other.

It has been found that the addition of 0.7 c.c. of 0.1*N* potassium hydroxide solution to 100 c.c. of a neutral culture medium considerably retards the growth of *Aspergillus*.

In the case of acids, the following limiting values have been obtained:

	Normal solutions of		
	Hydrochloric.	Sulphuric.	Acetic.
<i>Aspergillus</i>	10.5	17.0	21.0 c.c.
<i>Penicillium</i>	18.1	18.0	21.8 c.c.

per 100 c.c. of culture solution.

J. J. S.

Chemical Reactions occurring during Alcoholic Fermentation. III. EDUARD BUCHNER and JAKOB MEISENHEIMER (*Ber.*, 1906, 39, 3201—3218. Compare Abstr., 1904, ii, 199; 1905, ii, 274).—The authors, who have previously advanced the view that lactic acid is an intermediate product in the cell-free fermentation of sugars, do not consider the experiments of Sclator (*Trans.*, 1906, 89, 141) conclusive.

They have now investigated other by-products of cell-free

fermentation of sugars. Succinic acid is formed when living yeasts are used; when the fermentation is conducted with cell-free yeast juice, no succinic acid is formed. Glycerol was formed in the latter case.

The origin of glycerol in alcoholic fermentation is discussed.

When sugar is submitted to cell-free fermentation, the weight of sugar which disappears is much greater than the sum of the weights of alcohol and carbon dioxide obtained (Macfadyen, Morris, and Rowland, Abstr., 1901, i, 59). The conclusion of Harden and Young (Abstr., 1904, i, 543) that a portion of the sugar during cell-free fermentation is converted into a form which is not reducible, but becomes so by hydrolysis with hydrochloric acid, has appeared to the authors of such fundamental importance that they have repeated the experiments in question, using, however, bottom yeast. The results of Harden and Young are confirmed, and the conclusion drawn that the formation of a non-reducing sugar is due to an enzyme in the yeast juice.

Only a trace of amyl alcohol is formed during the cell-free fermentation of sugar. A. McK.

Studies on Putrefaction. LEO P. RETTGER (*J. Biol. Chem.*, 1906, 2, 71—86).—Putrefaction is the work of anaërobes only, judging from the organisms hitherto examined. The best known are *Bacillus putrificus* and the bacilli of malignant cedema and symptomatic anthrax. Bacteria of this type are generally absent from fæces. *B. enteriditis sporogenes* may be in part responsible for faecal putrefaction. *B. coli communis* and *B. lactis aerogenes* are not regarded as harmful, but protective, checking putrefaction. W. D. H.

Action of Ozone on Germinating Seeds. H. MICHEELS and P. DE HEEN (*Bull. Acad. roy. Belg.*, 1906, 364—367).—Ozone has an injurious effect on the growth of seedlings; the influence is especially marked on the roots. P. H.

Stimulating Action of Manganese on Germination. H. MICHEELS and P. DE HEEN (*Bull. Acad. roy. Belg.*, 1906, 288—289).—Colloidal solutions of manganese have a slightly more stimulating effect on germinating plants than similar solutions of tin. P. H.

Exchanges of Gas in a Green Plant grown in Light without Carbon Dioxide in Artificial Soil containing an Amide. JULES LEFÈVRE (*Compt. rend.*, 1906, 143, 322—324. Compare this vol., ii, 245).—In absence of carbon dioxide, a green plant supplied with amides (tyrosine, glycine, alanine, and leucine) can develop, and the dry matter increase to three times the initial amount, without liberation of oxygen. N. H. J. M.

Assimilation of Carbon Dioxide. WALTHER LÖB (*Chem. Centr.*, 1906, ii, 692; from *Landw. Jahrb.*, 35, 541, 578. Compare Abstr., this vol., ii, 43).—After long continued action of the silent electric discharge the formation of glycolaldehyde from mixtures of carbon monoxide and water-vapour with or without the presence of hydrogen

was observed. Acetaldehyde and water-vapour yield carbon monoxide and methane, the latter giving hydrogen by further decomposition. Carbon monoxide reacts to some extent with water to form hydrogen, carbon dioxide, formic acid, and formaldehyde. From ethyl alcohol, carbon dioxide, and water-vapour, β -acrose was obtained; it appears to be formed from glycolaldehyde as an intermediate product. The aldehyde is also formed when the carbon dioxide in the preceding mixture is replaced by the monoxide, and further from acetaldehyde and water. Acetic acid and water yield approximately equal quantities of methane and carbon dioxide with smaller quantities of carbon monoxide and hydrogen, which represent the chief products if a large excess of water is present. Methane and water-vapour yield higher hydrocarbons, hydrogen, and carbon monoxide. In presence of carbon dioxide, hydrogen and carbon monoxide are the chief products.

The application of the observed facts to biological processes is discussed.

H. M. D.

Thermochemical Theory of Assimilation. JULIUS FISCHER (*Zeit. Elektrochem.*, 1906, 12, 654—657).—A plant cell is regarded as a kind of heat engine in which the chlorophyll is kept at a higher temperature (by absorption of radiant energy) than the cell wall. The equilibrium in the circulating plasma is supposed to be displaced by alternate heating and cooling by contact with the chlorophyll and the cell wall.

T. E.

Assimilative Function of Carotin and the Second Assimilative Maximum at F. FRIEDRICH G. KOHL (*Chem. Centr.*, 1906, ii, 442—443; from *Ber. Deut. bot. Ges.*, 1906, 24, 222—229).—The colouring matter etiolin, supposed to occur in etiolated leaves, does not exist. Only traces of xanthophyll occur in addition to carotin. In spite of the absence of chlorophyll, etiolated leaves can, under certain conditions, assimilate and generate the oxygen which is necessary for the production of chlorophyll. Carotin also is able to decompose carbon dioxide with formation of oxygen. Both carotin and xanthophyll are best able to employ bluish-violet light, a fact which explains Engelmann's observation that the assimilation curve shows a second maximum at the F line of the spectrum.

P. H.

Manganese and the Development of Plants. I. GIOVANNI SALOMONE (*Chem. Centr.*, 1906, ii, 532; from *Staz. speriment. agrar. ital.*, 1906, 38, 1015—1024).—Although a certain quantity of manganese has a beneficial influence on the development of the plant as a whole, large quantities are toxic. The toxic effect of manganic salts is greater than that of manganous salts, and is dependent on the amount of dissociation, so that it is naturally greater for the salts of the more highly ionised mineral acids than for those of the organic acids; in other respects the poisonous effect is but slightly influenced by the nature of the anion. The very marked poisonous properties of barium manganate and permanganate are attributed to the combined influence of the barium and the manganese. Manganic acid is more

poisonous in the free state than in combination. Small quantities of manganous iodide exert a favourable influence on the germination of cabbage or carrot seeds.
P. H.

Chemical Processes in Frozen Plants. H. GORKE (*Landw. Versuchs-Stat.*, 1906, 65, 149—160).—Freezing of plants causes an intramolecular migration in the proteids, frequently accompanied by precipitation of a portion of the soluble proteid. Other changes no doubt occur.
N. H. J. M.

The Cell Membrane and its Constituents. JOSEF KÖNIG, AUG. FÜRSTENBERG, and RUDOLF MURFIELD (*Landw. Versuchs-Stat.*, 1906, 65, 55—110).—"Crude fibre" is a mixture of three groups of substances, the cellulose group soluble in copper-ammonium hydroxide, and containing 44·44—46·0 per cent. of carbon; the oxidisable (hydrogen peroxide and ammonia) portion of the lignin group, containing 55—60 per cent. of carbon; and cutin, which contains a still higher percentage of carbon.

The portion of the fibre which dissolves in copper-ammonium hydroxide contains more than 44·44 per cent. of carbon owing to the presence of methyl- or methoxy-groups. These are also present in lignin, but not in cutin. This lends support to the assumption of Cross and Bevan that a genetic relation exists between cellulose and lignin. Lignin, which is a mixture of several compounds, contains ethoxy-groups in addition to methyl. Cutin contains 68—70 per cent. of carbon and is mostly hydrolysed by alkali.

The amount of lignin increases with the age of the plant more than that of cellulose; the amount of cutin seems to have no definite relation to growth.

The utilisation of cell-membrane in foods by sheep is in inverse relation to the amount of lignin and cutin. Lignin is much less digested than cellulose, whilst cutin seems to be quite indigestible, except, perhaps, in the case of quite young plants.
N. H. J. M.

Fermentative Decomposition of Fats [by Enzymes]. SERGIUS FOKIN (*Chem. Rev. Fett. Harz. Ind.*, 1906, 13, 130—133; 163—166; 192—194; 219—221; and 238—240. Compare Abstr., 1904, i, 1071; ii, 199, 280).—Further results are given of the decomposition of fats by the enzyme contained in certain seeds such as flax, celandine, and castor-oil seeds. Under favourable conditions, the extent of the decomposition may amount to 99 per cent. of that required by theory. Flax and castor-oil seeds decompose tallow, cocoanut oil, olive oil, and linseed oil, almost completely, and the reaction is more complete on a large than on a small scale.
W. P. S.

Is Homogentisic Acid formed in Seedlings by the Decomposition of Tyrosine? ERNST SCHULZE and NICOLA CASTORO (*Zit. physiol. Chem.*, 1906, 48, 396—411. Compare Bertel, Abstr., 1903, ii, 321).—Homogentisic acid could not be detected in either fresh or chloroformed seedlings. The reactions observed by Bertel are not characteristic of homogentisic acid only, but are given by numerous other substances.
J. J. S.

Medicinal and Useful Plants of Brazil. THEODOR PECKOLT (*Chem. Centr.*, 1906, ii, 691; from *Ber. Deut. pharm. Ges.*, 16, 231—248. Compare this vol., ii, 701).—Analyses are given of parts of *Hura crepitans*, *Dalechampia Peckoltiana*, *Euphorbia prunifolia*, *E. Tirucalli*, and *Pedilanthus retusus*. H. M. D.

Chemical and Physiological Examination of the Fruit of *Chailletia toxicaria* (a West African poison). FREDERICK B. POWER and FRANK TUTIN (*J. Amer. Chem. Soc.*, 1906, 28, 1170—1183).—An investigation of the fruits of *Chailletia toxicaria* has shown that their poisonous properties are not due to an alkaloid, soluble proteid, or a cyanogenetic glucoside such as has been isolated from *Chailletia cymosa* (*Bull. Imp. Inst.*, 1903, 1, 14).

On extracting the fruits with light petroleum, 1.83 per cent. of a brown fat was obtained, consisting of oleodistearin and a residue, which on hydrolysis with alcoholic potassium hydroxide yielded (1) a small quantity of phytosterol, or a mixture of substances of this class melting at 135—148°, (2) stearic and oleic acids, the latter probably associated with an acid of a higher degree of unsaturation, and (3) very small quantities of formic and butyric acids.

After removing the fat, the fruit was extracted with alcohol, and on concentrating and adding water a resinous substance was obtained in quantity amounting to 2.5 per cent. of the weight of the fruit. By successive extraction with chloroform, ethyl acetate, and alcohol, the resin was separated into fractions which differed in their physiological action. On concentrating the aqueous liquid, which had been separated from the resinous substance and afterwards freed from tannic acid and colouring matter, a viscous syrup was obtained which contained a large amount of dextrose and an extremely poisonous principle which could not be isolated.

The results of the investigation lead to the conclusion that the fruit of *Chailletia toxicaria* contains at least two active principles, one of which causes cerebral depression or narcosis, and the other, cerebral excitation, leading to epileptiform convulsions. The latter poison is very slowly excreted, and produces a cumulative effect. E. G.

Cyanogenesis in Plants. Part IV. Occurrence of Phaseolunatin in Common Flax. WYNDHAM R. DUNSTAN, THOMAS A. HENRY, and SAMUEL J. M. AULD (*Proc. Roy. Soc.*, 1906, 78, B, 145—152. Compare Abstr., 1904, ii, 71).—The amount of phaseolunatin, which is very small in flax seeds, increases in the young plants until they reach the height of two or three inches. The amount then diminishes and finally disappears. The purified extract, from which the flax glucoside was obtained, was found to contain a considerable amount of potassium nitrate (compare Treube, *Ann. Jard. Bot. Buitenzorg*, 1905, 86); and one extract yielded a small amount of a sugar, probably raffinose.

The enzyme of flax which seems to be identical with that of *Phaseolus lunatus* is of the emulsin type; but it shows some well-marked differences from emulsin. N. H. J. M.

Cyanogenesis in Plants. Part V. Occurrence of Phaseolunatin in Cassava. WYNDHAM R. DUNSTAN, THOMAS A. HENRY, and SAMUEL J. M. AULD (*Proc. Roy. Soc.*, 1906, **78**, *B*, 152—158. Compare preceding abstract).—The glucoside of the root of bitter cassava (and doubtless also of sweet cassava) is identical with phaseolunatin. The enzyme of cassava closely resembles, and is probably identical with, that of the seeds of *Phaseolus lunatus* and young flax plants.
N. H. J. M.

New Examples of Rosaceæ Furnishing Hydrogen Cyanide. LÉON GUIGNARD (*Compt. rend.*, 1906, **143**, 451—458. Compare Abstr., 1905, ii, 604, 752; this vol., ii, 118, 119, 301).—The leaves of *Photinia serrulata* contain a cyanogenetic glucoside; the amount of hydrogen cyanide obtained from the leaves is greatest in the case of the leaf buds (0.170 per cent.), diminishes with the age of the leaf, and becomes approximately constant (0.132 per cent.) in leaves of a year old; the stem yields 0.030 to 0.011 per cent. of hydrogen cyanide, but negative results were obtained with the root; the leaves of *P. benthamiana* and *P. variabilis* also yield hydrogen cyanide.

The leaves, stems, and roots of eleven species of the *Cotoneaster* family, *C. affinis*, *C. multiflora*, *C. horizontalis*, *C. bacillaris*, *C. vulgaris*, *C. frigida*, *C. buxifolia*, *C. microphylla*, *C. thymifolia*, *C. Francheti*, and *C. pannosa*, and of two species of the *Spiraea* family, *S. Lindleyana* and *S. prunifolia*, were found to contain a cyanogenetic glucoside.

M. A. W.

Amount of Tyrosine in Seedlings of *Lupinus albus*. ERNST SCHULZE and NICOLA CASTORO (*Zeit. physiol. Chem.*, 1906, **48**, 387—395. Compare Bertel, Abstr., 1903, ii, 321; Schulze and Castoro, *ibid.*, 566).—The substance described by Bertel is not tyrosine, and his method of isolation is useless.

Seedlings of *Lupinus albus* two days old contain very little tyrosine, but as the reserve material is used up the amount of tyrosine increases. The tyrosine appears to be contained in the cotyledons, and not in the hypocotyledon or roots. An increase in the amount of tyrosine after chloroforming could not be detected.
J. J. S.

Constituents of the Poison Ivy Plant (*Rhus Toxicodendron*). SALOMON F. ACREE and W. A. SYME (*Amer. Chem. J.*, 1906, **36**, 301—321).—An ethereal extract of the leaves and flowers of *Rhus Toxicodendron* was investigated, and gallic acid, fisetin, rhamnose, and a poisonous, tarry substance were isolated. The poisonous substance is not volatile with acetic acid or alcohol. It is decomposed by hot acetic acid with formation of gallic acid, fisetin, and rhamnose, and yields a lead compound which is soluble in ether. A portion of the poisonous material can be precipitated by lead acetate from a solution of the purified, tarry substance in 50 per cent. alcohol. On decomposing the precipitate with hydrogen sulphide and extracting the liquid with ether, a yellow, poisonous resin is obtained, which is termed *toxicodendrin*. When the poison is applied to the skin, it produces itching and inflammation, but a cure can be easily effected by treating the

affected part with hot solution of potassium permanganate. A method is described for obtaining the poisonous substance directly from the plant.

E. G.

Enzymatic Action of Radishes. TADASU SAIKI (*Zeit. physiol. Chem.*, 1906, 48, 469—472).—Radishes when kept became sweet, owing to the transformation of starch into sugar. The juice of a radish contains a diastatic enzyme which converts starch into maltose. Radishes contain very little proteid, and no proteolytic ferment was found.

W. D. H.

Chemical Composition of Styrian Fruits. EDUARD HOTTER (*Chem. Centr.*, 1906, ii, 697—698; from *Zeit. Landw. Versuch.-Wesen. Oesterr.*, 9, 747—800).—The seed-fruits, apple, pear, quince, medlar, and mountain-ash yield a lævo-rotatory juice containing considerably more lævulose than dextrose. The three first contain frequently a considerable quantity of sucrose. The ash contains 48—53 per cent. K_2O , and but little alkaline-earth oxides. The juice from the stone-fruits, cherry, apricot, peach, and plum, contains nearly always more dextrose than lævulose. The juice from sweet and sour cherries is lævo-rotatory, that from the morello cherry, peach, and most kinds of plum, dextro-rotatory. The juice from the red-currant, gooseberry, strawberry, raspberry, blackberry, and bilberry is lævo-rotatory, and contains more lævulose than dextrose, although the difference is small. Sucrose is only present in small amount, sometimes not at all, and the ash contains a smaller proportion of potassium, but more calcium, magnesium, and phosphoric acid than the ash of seed and stone fruits.

H. M. D.

Effect of Sterilising Soil on the Development of Plants. CARL SCHULZE (*Landw. Versuchs-Stat.*, 1906, 65, 137—147. Compare Abstr., 1905, ii, 54).—The sterilisation of soils results in the production of substances injurious to plants, and in increased availability of soil constituents, and the effect on plants depends on the predominance of the one over the other. It is desirable to employ a variety of soils and a variety of plants in experiments on the effect of sterilisation.

N. H. J. M.

Relative Value of Different Phosphates. DMITRI PRIANISCHNIKOFF (*Landw. Versuchs-Stat.*, 1906, 65, 23—54. Compare Abstr., 1899, ii, 514).—Sand culture experiments showed that the phosphoric acid of straw ash, which had been extracted with water, was equal to potassium dihydrogen phosphate. The effect of bone meal was about 50 to 60 per cent. of that obtained with soluble phosphates. As regards crude phosphates, lupins manured with a phosphorite, resembling apatite, showed considerable development, whilst gramineous plants grew very little. In soils, the influence of acidity may exceed all others and equalise the action of different phosphates. The employment of ammonium salts in sand cultures renders the most sparingly soluble phosphates available to all plants.

Ammonium nitrate seems to be more favourable to maintaining neutral conditions than other nitrogenous manures; it is, however, not entirely without effect on the assimilability of phosphates.

N. H. J. M.

Analytical Chemistry.

Extraction Apparatus. J. DOCTERS VAN LEEUWEN (*Chem. Centr.*, 1906, ii, 389; from *Chem. Weekblad.*, 1906, 3, 372—373).—The capsule containing the substance is suspended by means of a copper wire passing through the reflux condenser, and after immersion for half an hour in the boiling liquid it is raised and suspended in the vapour. After one hour's extraction in this position, an adapter is attached for distilling off the solvent. P. H.

New Automatic Pipette. STEIN (*Chem. Zeit.*, 1906, 30, 967).—The pipette, which is filled by means of a spray bellows, is particularly suitable for use with alkalis. A sketch of the apparatus is appended. P. H.

Methods for Preparing Normal Acids. J. G. MASCHHAUPT (*Chem. Centr.*, 1906, ii, 358; from *Chem. Weekblad.*, 3, 357—367).—The best results are obtained by checking the acid with heated sodium carbonate (Merck). The method based on the distillation of ammonium sulphate also gives good results. L. DE K.

Estimation of Halogens in Organic Substances. HUGO SCHIFF (*Zeit. anal. Chem.*, 1906, 45, 571—572).—A reply to Sadtler (*Abstr.*, 1905, ii, 760). The author calls attention to his own process published twenty-eight years ago (*Abstr.*, 1879, 555), which he still upholds. L. DE K.

Estimation of Halogens in Organic Substances. LESLIE HAMILTON BERRY (*Chem. News*, 1906, 94, 188).—About 0.2 gram of the compound is weighed in a small platinum crucible, which is then filled with a mixture of one part of anhydrous sodium carbonate and five parts of calcium oxide. When iodine has to be estimated, sodium carbonate only should be used. The crucible is then inverted in a larger platinum crucible, and the space between the two is filled up with the same sodium carbonate-lime mixture.

The larger crucible is then heated with the blowpipe, commencing at the bottom, until the whole is red hot. After half an hour's heating the mass is allowed to cool, and is then decomposed with a sufficiency of cold dilute nitric acid (1:4). The halogen is now estimated by adding an excess of *N*/10 silver nitrate and estimating

the silver in the filtrate by Volhard's thiocyanate process with iron-alum as indicator. The test-analyses with chloral, iodoform, and dibromobenzene show the accuracy of the method. L. DE K.

Elimination and Alkalimetric Estimation of Silicon Fluoride in the Analysis of Fluorides. ALBERT HILEMAN (*Amer. J. Sci.*, [iv], 22, 329—338).—The various methods for the volumetric estimation of silicon fluoride have been examined and compared. When the silicon fluoride is absorbed by an alcoholic solution of potassium chloride, and the hydrochloric acid liberated according to the equation $3\text{SiF}_4 + 4\text{H}_2\text{O} + 4\text{KCl} = 2\text{K}_2\text{SiF}_6 + \text{H}_4\text{SiO}_4 + 4\text{HCl}$ is titrated with alkali, much larger values are found than when the fluoride is allowed to act on water and the solution titrated with alkali in accordance with the equations $3\text{SiF}_4 + 4\text{H}_2\text{O} = 2\text{H}_2\text{SiF}_6 + \text{H}_4\text{SiO}_4$, $2\text{H}_2\text{SiF}_6 + 12\text{KOH} = 12\text{KF} + 2\text{H}_4\text{SiO}_4 + 4\text{H}_2\text{O}$. The higher values obtained by the first process are due to the presence of hydrofluoric as well as hydrofluosilicic acid in the alcoholic solution.

The difficulty of eliminating the whole of the fluorine as silicon fluoride has been confirmed, and an apparatus is described in which the fluoride may be boiled with sulphuric acid and regular results of a fair degree of accuracy obtained. For details of the method and a description of the apparatus the original must be consulted. The difficulty of removing all the fluorine is traced to small quantities of water in the decomposition vessel, necessitating the use of carefully prepared sulphuric acid and of ignited silica or quartz. H. M. D.

Titration of Hydrofluosilicic Acid. N. SAHLBOM and F. WILLY HINRICHSSEN (*Ber.*, 1906, 39, 2609—2611).—The Kaiserbad thermal springs in Aachen were found to contain 0.00080 gram of fluorine per litre. Penfield's method (*Abstr.*, 1879, 829), based on the reaction $\text{H}_2\text{SiF}_6 + 2\text{KOH} = \text{K}_2\text{SiF}_6 + 2\text{H}_2\text{O}$, was employed. Since hydrofluosilicic acid undergoes hydrolytic dissociation with great ease in the presence of hydroxyl ions, it is necessary, after precipitating the potassium or the barium salt by the addition of alcohol, to protect the salt from the action of hydroxyl ions, otherwise the titration cannot be effected according to the equation given. If the solution to be titrated is, however, heated, the amount of hydrolytic dissociation is increased, and the reaction proceeds according to the equation $\text{H}_2\text{SiF}_6 + 6\text{KOH} = 6\text{KF} + \text{Si}(\text{OH})_4 + 2\text{H}_2\text{O}$. A. McK.

Estimation of Oxygen in Salt Solution. JOSEPH BARCROFT and PHILIP HAMILL (*J. Physiol.*, 1906, 34, 300—314).—In determinations of the respiration of organs, it is important to know the amount of oxygen in the salt solution usually employed for perfusion. This can be easily effected with a simple adaptation of the mercurial pump which is fully described, and the error is 3 or 4 per cent. of the quantity of oxygen measured when the estimation is made with 10 c.c. of salt solution. W. D. H.

Estimation of Sulphur in Sulphides. VON NOSTITZ (*Chem. Centr.*, 1906, ii, 702; from *Zeit. Chem. Apparatenkunde*, 1, 460—461).—Five grams of the sample are dissolved in boiling dilute hydrochloric

acid (1:1), and the hydrogen sulphide evolved is passed first through an empty cylinder and then through another containing a 10 per cent. solution of potassium hydroxide. For a full description of the apparatus, the illustration in the original should be consulted.

The hydrogen sulphide absorbed by the alkali is then estimated by cautiously acidifying with dilute sulphuric acid and titrating as usual with iodine solution (7.9 grams of iodine and 20 grams of potassium iodide per litre). One c.c. of this represents 0.0022 per cent. of sulphur.

L. DE K.

Iodometric Estimation of Hydrogen Sulphide. OTTO BRUNCK (*Zeit. anal. Chem.*, 1906, **45**, 541—551).—A series of experiments showing that hydrogen sulphide cannot be titrated satisfactorily either in neutral or alkaline solution. Even on adding the iodine solution very rapidly, the loss is still very considerable. If, however, the hydrogen sulphide solution is added to a measured quantity of standard iodine, as recommended by Fresenius, until the liquid is decolorised, the very slight excess of hydrogen sulphide may then be titrated accurately.

Good results may also be obtained by adding the solution to an excess of standard iodine and then titrating with thiosulphate. Should the liquid be alkaline, a sufficiency of acid should be added before the titration. Soluble sulphides may be titrated by either method, and *N*/100 iodine solution will be found the most suitable. Strong solutions of hydrogen sulphide should be diluted suitably with air-free water.

L. DE K.

Estimation of Carbon Disulphide and Total Sulphur in Commercial Benzene. EDWARD S. JOHNSON (*J. Amer. Chem. Soc.*, 1906, **28**, 1209—1220).—*Carbon Disulphide.*—The carbon disulphide is converted into potassium xanthate by addition of saturated alcoholic potassium hydroxide; this is removed from the benzene by repeated washings with alkaline water, and the xanthate is then converted into the copper compound by slightly acidifying with acetic acid and precipitating with copper sulphate. The precipitate is collected, washed, and ignited to oxide. In practice, one part of oxide = 1.75 of carbon disulphide.

Estimation of Total Sulphur.—Five c.c. of the sample are introduced into a small vaporiser, through which is passed a slow current of hydrogen; this and the benzene vapour are then burnt in a special apparatus in oxygen, and the products of combustion are absorbed in bottles containing sodium carbonate and bromine solution; this causes a complete conversion of the sulphur into sulphuric acid, which may then be estimated gravimetrically. If it is preferred to make a volumetric estimation, the products of combustion may be collected in a standard solution of sodium hydroxide, and after adding some neutral hydrogen peroxide the excess of alkali is titrated with standard acid.

L. DE K.

Estimation of Urinary Sulphur. ALBERT DESMOULIÈRE (*J. Pharm. Chim.*, 1906, [vi], **24**, 294—300).—For the estimation of total sulphur the methods described by Moreigne (*Abstr.*, 1895, ii, 327)

and Modrakowski (Abstr., 1903, ii, 611) are recommended in preference to those suggested by Mohr (Abstr., 1895, ii, 528) and by Folin (Abstr., 1902, ii, 352). The sodium peroxide used in Modrakowski's process should be tested for sulphate, since commercial samples sometimes contain this impurity.

The "total acid sulphur" is estimated by boiling 100 c.c. of urine with 10 c.c. of hydrochloric acid and precipitating in the usual way with barium chloride. The "sulphur as ethereal sulphates" is determined by adding 125 c.c. of a mixture of baryta water (2 parts) with a saturated solution of barium chloride (1 part) to 125 c.c. of urine. To 200 c.c. of the filtrate 20 c.c. of hydrochloric acid is added, and the mixture is boiled for fifteen minutes. The precipitate of barium sulphate thus formed is filtered and weighed.

The difference between "total acid sulphur" and "sulphur as ethereal sulphates" is taken as the "sulphate."

Baumann's process for the estimation of sulphates in urine, which depends on precipitation by barium chloride at 100° in presence of acetic acid, gives inaccurate results owing to the inclusion with the sulphate of barium urate and phosphate. The latter persistently adheres to the precipitate of barium sulphate, and cannot be entirely removed even by washing with boiling dilute hydrochloric acid. Further, there is probably a partial decomposition of the ethereal sulphates when the urine is heated with acetic acid at 100° so that a portion of these is also returned as sulphates.

T. A. H.

[Estimation of] Sodium Sulphite in Foods. CLIFFORD D. HOLLEY (*J. Amer. Chem. Soc.*, 1906, 28, 993—997).—A series of experiments showing that the amount of sulphur dioxide recoverable from foods preserved by means of sulphites by distillation with phosphoric acid is about one-fourth of the quantity originally present.

L. DE K.

Estimation of Small Quantities of [Combined] Sulphuric Acid in Waters. GUSTAVE BRUHNS (*Zeit. anal. Chem.*, 1906, 45, 573—584).—A slight modification of the barium chromate method. To 150 c.c. of water are added 5 c.c. of 10 per cent. barium chromate emulsion and 1 c.c. of hydrochloric acid, and the whole is frequently shaken for half an hour. After neutralising with ammonia and diluting to 200 c.c., the liquid is filtered, and 100 c.c. of the filtrate are treated in a closed flask with potassium iodide and a little hydrochloric acid. After half an hour, the liberated iodine is titrated with thio-sulphate solution. This should be of such a strength that 20.76 c.c. represent the iodine liberated from potassium iodide by 10 c.c. of $N/10$ permanganate.

On account of the slight solubility of barium chromate in water, 0.15 c.c. of thiosulphate is allowed for. One c.c. of the latter represents 1.78 mg. of sulphuric anhydride.

L. DE K.

Analysis of Dithionic Acid and the Dithionates. R. HARMAN ASHLEY (*Amer. J. Sci.*, 1906, [iv], 22, 259—262).—The dithionate is dissolved in water, excess of sulphuric acid is added, and the whole is

distilled in a current of carbon dioxide until sulphuric fumes begin to appear. The sulphur dioxide given off during the distillation owing to the decomposition of the dithionic acid is absorbed in standard iodine solution, the excess of iodine being titrated as usual with thiosulphate. Hydrochloric acid should not be employed instead of sulphuric acid. In the course of the investigation it appeared that barium dithionate crystallises, not with $4\text{H}_2\text{O}$, but with $2\text{H}_2\text{O}$. It also does not effloresce readily, as has been stated.

L. DE K.

Sources of Error in the "Citrate Process" for the Estimation of Phosphoric Acid in Mineral Phosphates. HENRI PELLET (*Ann. Chim. anal.*, 1906, 11, 331—332. Compare Abstr., 1905, ii, 353).—When employing this process, it is absolutely necessary to remove any soluble silica. This is done effectually and in a few minutes by moistening the powdered sample with strong hydrochloric acid and drying on a sand-bath. The authors, however, prefer the weighing directly as ammonium phosphomolybdate. L. DE K.

Estimation of Arsenic when in Minute Quantities. WILLIAM THOMSON (*Mem. Manchester Phil. Soc.*, 1906, 50, (12), 3—14).—Comparative experiments on the estimation of arsenic by the electrolytic and the Marsh-Berzelius methods have shown that the size of the arsenic mirror obtained by the former method is diminished to a considerable extent if nitrogen compounds are present.

Using different metals as cathodes in the electrolytic estimation of arsenic when present in the form of arsenious acid, the mirrors obtained with lead, graphite, iron, and cadmium corresponded with 100, 90, 80, and 30 per cent. respectively of the amount of arsenic obtained with a cathode of pure zinc. When the arsenic was present in the form of arsenic acid, zinc, lead, iron, cadmium, and graphite cathodes gave respectively 90, 90, 50, 25, and 10 per cent. of the total arsenic present.

Using zinc alloys containing 0.5 per cent. of nickel, cobalt, copper, or iron in the Marsh-Berzelius apparatus, it was found that the three first-mentioned gave the full amount of arsenic, whereas a mirror corresponding only with 15 per cent. was obtained with the iron alloy. On addition of cadmium sulphate, this was increased to 50 per cent.

H. M. D.

Estimation of Arsenic Acid. LEOPOLD ROSENTHALER (*Zeit. anal. Chem.*, 1906, 45, 596—599).—The author has noticed that in the presence of a large excess of hydrochloric or sulphuric acid, arsenic acid liberates iodine from potassium iodide quantitatively; the iodine may then be titrated with thiosulphate.

About 0.3 gram of the sample is dissolved in a little water, 2 grams of potassium iodide are added, and then 25 per cent. hydrochloric or 50 per cent. sulphuric acid until a precipitate begins to form, which is then redissolved by cautious addition of water. After waiting for at least ten minutes, the iodine liberated is titrated.

An indicator is not required. One c.c. of $N/10$ thiosulphate = 5.75 mg. of As_2O_5 .

L. DE K.

Estimation of Carbon in Iron-Alloys. ÉMILE JABOULAY (*Chem. Centr.*, 1906, ii, 164—165; from *Rev. gen. Chim. pure appl.*, 9, 178—180).—The alloy is burnt in a current of oxygen, generated by the action of water on “oxylith,” and the carbon dioxide formed is absorbed with the usual precautions and weighed. A Heraeus electric furnace is employed. Ferrotungsten, ferrovanadium, and ferrotitanium burn readily; ferrochrome, ferrosilicon, ferromanganese, and ferromolybdenum should be mixed with bismuth oxide in order to facilitate the oxidation. L. DE K.

Use of a Layer of Copper Oxide or Copper Oxide and Asbestos 5 cm. in Length in Elementary Organic Analysis. J. MAREK (*J. pr. Chem.*, 1906, [ii], 74, 237—240. Compare this vol., ii, 496).—A reply to the criticisms of Dennstedt (this vol., ii, 632. The greater length of time required for the combustion of small amounts of substance, such as 0.5 gram, when using copper oxide instead of sheet platinum, is negligible. G. Y.

Two New Forms of Apparatus in Organic Analysis. ERWIN RUPP (*Zeit. anal. Chem.*, 1906, 45, 558—561).—*Azotometer*.—A modification of Schiff's apparatus by which regurgitation of the lye into the combustion tube is entirely prevented.

Potash Apparatus.—Most of the numerous improvements on Liebig's original potash bulbs cause an undesirable pressure inside the combustion tube. In the author's apparatus, which somewhat recalls the analyser of a Coffey's still, the pressure does not exceed that in the ordinary form of potash bulbs. L. DE K.

Estimation of Volatile Combustible Matters in Coals and Lignites. E. E. SOMERMEIER (*J. Amer. Chem. Soc.*, 1906, 28, 1002—1013).—A large number of experiments showing that the estimation of volatile matter in coal is largely affected by the method of heating, the fineness of the sample, and the amount of loosely held moisture. In bituminous coals the differences do not exceed 3 or 5 per cent., but in lignites they may reach even 25 per cent., owing chiefly to mechanical loss during the expulsion of the volatile matter. L. DE K.

Estimation of Ash [of Coal] in Electrically Heated Organic Combustion Furnaces. H. SEIBERT (*Chem. Zeit.*, 1906, 30, 965—966).—The author approves of the electric furnace as source of heat for the estimation of ash in coals. Owing to less danger of volatilisation the results are usually a little higher than by the ordinary methods. A porcelain boat is preferable to one made of platinum, but should also be reweighed frequently. L. DE K.

Estimation of Carbon Dioxide and Carbon. JOHN MCFARLANE and ARNOLD W. GREGORY (*Chem. News*, 1906, 94, 133—134).—The apparatus consists of a wide filter tube closed by a small piece of rubber tube and a clip. A plug of glass-wool is inserted into the base of the wider part and covered by a layer of asbestos pulp, which is then kept steady by covering it with some broken glass. The mouth

of the tube is fitted with a doubly-perforated rubber cork through one hole of which passes a glass tube (*b*) bent and constricted at its lower end and enlarged at the top. Through the other opening passes a spirally bent tube which terminates in the same form as tube (*b*), except that a small inverted U-tube is fused inside.

The apparatus is connected to the combustion tube, or evolution flask, and a current of purified air is passed through to free it from any carbon dioxide. The rubber stopper in the mouth of *b* is temporarily removed, and a measured quantity of standardised barium hydroxide is introduced so as to fill the filter tube and partly the spiral. The current of air is again passed through, causing some of the liquid to pass through the inverted U-tube. The carbon dioxide resulting from the combustion of the carbon, or the decomposition of carbonates, is now passed through the apparatus and fully absorbed by the barium hydroxide. The clip is now opened, the filtrate is collected, and the apparatus rinsed repeatedly with hot water containing a drop of phenolphthalein. The filtrate is then titrated. It must be remarked that this method works satisfactorily with minute quantities of carbon, but fails when the amount of carbon dioxide increases.

The barium carbonate formed in the reaction is then dissolved in dilute hydrochloric acid and finally weighed as sulphate.

Another process is given by means of which larger amounts of carbon dioxide may be estimated with accuracy. Briefly, it is as follows: The carbon dioxide is passed through two flasks containing an ammoniacal solution of barium chloride which has been boiled and filtered. At first but little barium carbonate is formed, but on boiling the contents of the first flask, when the steam evolved heats the contents of the second flask sufficiently, barium carbonate is precipitated quantitatively. When cold, the liquid is filtered through an asbestos filter, and the well-washed barium carbonate is finally converted into sulphate and weighed. There is no danger of any source of error due to the action of atmospheric carbon dioxide during the filtration, as this gives no immediate precipitate with ammoniacal barium chloride in the cold.

L. DE K.

Estimation of Silica. NICHOLAS KNIGHT and F. A. MENNEKE (*Chem. News*, 1906, 94, 165—166).—A series of experiments showing that silica in siderite and dolomite may be readily estimated by boiling the finely-powdered material with dilute hydrochloric acid (1:1). In the case of siderite, dilute nitric acid may be used advantageously. The insoluble matter is collected, ignited, and weighed, and then treated in the usual manner with sulphuric and hydrofluoric acids, when the loss represents the silica. No perceptible amount of silica passes into the solution.

In the case of hæmatite, limonite, and pyrolusite, a considerable amount of silica passes into the solution, and must be recovered in the usual manner.

L. DE K.

A System of Qualitative Analysis, including nearly all the Metallic Elements. ARTHUR A. NOYES (*Chem. News*, 1906, 93, 134—136, 146—149, 156—160, 171—175, 179—181, 189—192,

205—207, 216—218, 226—227, 239—240, 250—252, 262—263; from *Technology Quarterly*, 17, [3].—A lengthy article, unsuitable for condensation, divided into five parts, namely, the preparation of the solution, the tungsten and niobium group, the selenium and silver groups, the platinum group, and the detection of lead and tellurium, the ruthenium, iridium, copper, and molybdenum groups, and the other members of the rare earth, aluminium and iron, alkaline earth and alkali groups.

As a solvent, nitric acid is used in preference to hydrochloric acid. Any undissolved matter is then treated with hydrochloric or nitrohydrochloric acid, except in the case of non-metallic compounds, when hydrofluoric acid is used, the excess of which is, if necessary, got rid of by evaporation with nitric acid and silica. Insoluble matters are rendered soluble by fusion with sodium peroxide, sodium carbonate, and sulphur, potassium pyrosulphate, &c.

For details, the processes and tables in the original article must be consulted. L. DE K.

Estimation of Potassium [by Tarugi's Method]. RAFFAELLO PAJETTA (*Gazzetta*, 1906, 36, ii, 150—156).—Contrary to Tarugi's statement (Abstr., 1904, ii, 590), the solubility of potassium persulphate in water is greatly influenced by the presence of other salts; sodium sulphate in particular greatly increases the solubility. In consequence of this, Tarugi's method of estimating potassium (*loc. cit.*) does not give accurate results: the author's determinations made by the method would indeed indicate that it is quite valueless. W. A. D.

Analysis of Sodium Peroxide. RICHARD LASEKER (*Chem. Centr.*, 1906, ii, 361; from *Oesterr. Chem. Zeit.*, [ii], 9, 164—166).—The Archbutt-Grossmann process (decomposition with dilute sulphuric acid in presence of cobalt nitrate and measuring the oxygen evolved) is recommended (compare Abstr., 1905, ii, 284). L. DE K.

Detection of the Metals of the Alkaline Earths by Spectrum Analysis in the Course of Qualitative Analysis. ERNST H. RIESENFELD and HANS E. WOHLERS (*Ber.*, 1906, 39, 2628—2631).—Instead of using the ordinary analytical methods for the detection of barium, strontium, and calcium, the authors recommend the spectrum method, which they conduct by the aid of the special burner they described recently (this vol., ii, 593). A. McK.

Reaction for Distinguishing Dolomite and Calcite. FELIX CORNU (*Centr. Min.*, 1906, 550).—Approximately equal amounts of the two minerals, in a powdered condition, are shaken in separate tubes with distilled water and a little phenolphthalein; the alkaline reaction of the calcite produces a dark red colour, whilst the colour in the tube containing the dolomite becomes only slightly reddish. L. J. S.

Precipitation of Barium as Sulphate, and its Separation from Calcium. ANTON SKRABAL and P. ARTMANN (*Zeit. anal. Chem.*, 1906, 45, 584—595. Compare this vol., ii, 126).—The solution of the

chlorides is neutralised with sodium carbonate and diluted to such an extent that there are at least 30 c.c. of liquid for every 0.1 gram of calcium oxide. The solution is heated to boiling and precipitated with $N/2$ sulphuric acid. The precipitate, which still contains calcium sulphate, is collected and washed as usual, then ignited and fused with a little sodium carbonate. The residue is treated with hot water and acidified with acetic acid with the usual precautions. A precipitate consisting of pure barium sulphate is thus obtained, and the filtrate from it is added to the first filtrate containing the greater part of the calcium sulphate.

L. DE K.

The Electrolytic Estimation of Copper. FRITZ FOERSTER (*Ber.*, 1906, 39, 3029—3035).—When the ordinary massive platinum cathode is employed, nitric acid is required in the copper solution in order to ensure a deposition of firmly adhering copper, and as the nitric acid itself becomes reduced at the cathode to ammonia, sulphuric acid must also be present to keep the solution acid. When a wire net cathode is used, the nitric acid may be omitted. With an *E.M.F.* of about 1.7 to 2 volts, copper can be precipitated quantitatively from its sulphate in dilute sulphuric acid solution, even in the presence of cadmium, zinc, nickel, cobalt, and iron, since these metals require more than 2 volts for their deposition. For this purpose an ordinary lead accumulator may be employed with an electrolytic cell, consisting of a glass beaker fitted with a wire net cathode and a platinum spiral anode. As each cell requires at the commencement only 0.12 ampere, several of these may be connected in parallel, and the depositions when started overnight are complete next morning. The time required to effect this deposition may be very materially shortened by the use of a hot electrolyte, and at 75° 0.15 gram of copper may be deposited in about one hour from a sulphuric acid with an *E.M.F.* of 2 volts.

When the operation is carried out in this way neither ammeter nor regulator is required; the completion of the deposition is shown by the cessation of the evolution of oxygen at the anode. G. T. M.

A Delicate Colour Reaction for Copper, and a Micro-chemical Test for Zinc. HAROLD C. BRADLEY (*Amer. J. Sci.*, [iv], 22, 326—328).—The dark blue compound, which hæmatoxylin yields with copper salts, can be used as an extremely sensitive colour test for copper. Comparative measurements indicate that under favourable conditions the limiting concentrations at which copper can be detected by the ferrocyanide, potassium iodide, and starch, and the hæmatoxylin reactions are represented by one part of copper in 10^{-5} , 10^{-6} , and 10^{-9} parts of water respectively.

For the detection of small quantities of zinc, the formation of zinc nitroprusside is recommended. The salmon-coloured precipitate consists of microscopic crystals which can be identified and distinguished readily from the amorphous precipitates formed by the other metals. In using the test for the detection of zinc in organic tissues, the ash is dissolved, and after removal of copper the solution is concentrated and digested with a drop of sodium nitroprusside solution on

a microscope slide. On cooling, rectangular plates and prisms of zinc nitroprusside are deposited.

H. M. D.

Separation of Iron and Manganese from Nickel and Cobalt by Treating the Sulphides with Dilute Acids. W. FUNK (*Zeit. anal. Chem.*, 1906, 45, 562).—The liquid which should contain about 0.1 gram of cobalt or nickel is diluted to 200 c.c. Four grams of ammonium chloride are added, and after heating, the metals are precipitated with ammonium sulphide, avoiding excess. When cold, *N*-formic acid is added until the liquid contains about 1 per cent. of free acid, and a current of hydrogen sulphide is passed through. The manganese and iron dissolve as formates, whilst the nickel and cobalt sulphides are left undissolved. From manganese, the separation is fairly accurate, but this is not so with iron. If iron should be present, it is advisable to remove it first by the ammonium formate process (this vol., ii, 707).

L. DE K.

New Reaction for Tin. C. REICHARD (*Chem. Centr.*, 1906, ii, 166—167; from *Pharm. Centr.-Halle*, 47, 391—394).—If a little powdered uric acid is moistened with a drop of stannic chloride, then with strong sodium hydroxide solution, and heated, a spot is obtained, varying in colour from grey to black, according to the amount of tin present. Stannous chloride does not give the reaction, neither do arsenic and antimonious acids. Lead and cadmium also give a negative result. Copper salts give a black precipitate. A mixture of mercuric chloride and uric acid gives, besides mercuric oxide, a reddish-brown product. Bismuth, however, gives the same reaction as tin, but the precipitate is insoluble in excess of sodium hydroxide. The black spot is soluble with difficulty in nitric or hydrochloric acid, but readily so in sulphuric acid.

L. DE K.

Some Reactions of Tervalent Titanium. HERMANN GROSSMANN (*Chem. Zeit.*, 1906, 30, 907).—With solutions containing trivalent titanium, potassium thiocyanate gives a black precipitate insoluble in excess, which gradually changes into titanous acid with evolution of hydrogen cyanide. Potassium ferrocyanide gives a reddish-brown precipitate rapidly changing to orange-yellow; on warming with acids it is slowly dissolved. Potassium ferricyanide gives a dark brown precipitate rapidly changing to green. Sodium nitroprusside gives a dark brown precipitate, soon changing to light brown with evolution of hydrogen cyanide. Sodium acetate causes a green coloration, and on boiling gives a greyish-blue precipitate changing to a light grey. Sodium formate behaves similarly in the cold, but on boiling, titanous acid is deposited. Soluble oxalates yield on heating insoluble double oxalates; they do not prevent the precipitation by alkalis. Normal gallates, xanthates, salicylates, and succinates also give precipitates on boiling.

Tartaric and citric acids do not affect the colour, but on adding excess of sodium hydroxide a dark blue liquid is obtained. Normal tartrates cause a precipitate soluble in excess and not precipitated by alkali hydroxides.

L. DE K.

Rapid Method of Estimating the Metals of the Arsenic Group, Exclusive of Gold or Platinum. O. MATERNE (*Chem. Centr.*, 1906, ii, 557; from *Bull. Soc. chim. Belg.*, 1906, 20, 46—68).—*Arsenic sulphide* dissolves slowly in a cold, but readily in a boiling two per cent. solution of borax, forming a light yellow liquid which remains clear even on cooling; the sulphide is precipitated from the solution in the form of pure yellow flakes on the addition of hydrochloric, acetic, tartaric, citric, formic, or carbonic acids, but the precipitation is only quantitative after the passage of hydrogen sulphide. *Antimony sulphide* is but slightly soluble in borax solution, the solubility being diminished by boiling the solution, but it dissolves in a boiling solution of sodium carbonate containing 5 per cent. of anhydrous, or 13.5 per cent. of the crystallised salt; the solution so obtained is clear while hot, but deposits the orange-brown sulphide on cooling; on adding acid or ammonium chloride the orange-red sulphide is precipitated, but the last traces are only deposited with the aid of hydrogen sulphide. *Stannous sulphide* is insoluble in cold borax solution and very slightly soluble in hot; it is insoluble in cold and only slightly soluble in hot sodium carbonate, but dissolves in vigorously boiling 10 per cent. sodium hydroxide; it is reprecipitated from this solution in brownish-red flakes on adding acid or ammonium chloride, but unless hydrogen sulphide is also employed the precipitation is not complete. *Stannic sulphide*, which may be either light yellow, brownish-yellow, or greenish-yellow, is insoluble in cold, but readily soluble in hot, borax solution; it dissolves readily in sodium carbonate and very readily in sodium hydroxide, and can be precipitated quantitatively from these solutions on acidifying and passing hydrogen sulphide.

These facts have been made use of in devising a new scheme of qualitative and quantitative analysis, for details of which the original paper should be consulted. The following is a rapid method of separating the sulphides of arsenic antimony and tin. The mixed sulphides are digested with a boiling solution of sodium carbonate; the residue on filtration is tin sulphide; the filtrate on cooling deposits a brown precipitate of antimony sulphide which becomes orange by dissolving in sodium carbonate and reprecipitating with acid. The filtrate from the brown precipitate of antimony sulphide yields arsenic sulphide on adding concentrated hydrochloric acid.

P. H.

Reactions of Empyreumatic Oil of Juniper (Oleum Cadi). CAMILLE PÉPIN (*J. Pharm. Chim.*, 1906, [vi], 24, 248—259. Compare this vol., ii, 633).—A number of genuine and sophisticated samples of this oil have been examined and compared with pinewood tar, and the true oil is found to have the following characteristics. It is fluid, possesses a smoky odour, floats on water, and its acidity, calculated as acetic acid, is less than 1.5 per cent. When distilled under atmospheric pressure, at least 65 per cent. should pass over between 150° and 300°, and from 70 to 75 per cent. between 10° and 215° under a pressure of 0.065 mm. These two fractions are smaller when the oil is adulterated with pinewood tar.

T. A. H.

Detection of Methyl Alcohol. E. VOISENET (*Bull. Soc. chim.*, 1906, [iii], 35, 748—760. Compare this vol., ii, 59).—The method,

which is specially suited to the detection of methyl alcohol in commercial ethyl alcohol, depends on the regulated oxidation of the sample by means of chromic acid mixture, so that the methyl alcohol present is converted into methylal, the ethyl alcohol furnishing at the same time acetaldehyde, acetic acid, ethyl acetate, and acetal. From the reaction mixture, the acetaldehyde is distilled off as a first fraction, and the second fraction, which will contain any methylal present, is used for testing by the colour reaction already described (*loc. cit.*), methylal giving the same violet coloration as formaldehyde. The test is said to be capable of detecting 1 part of methyl alcohol in 20,000 of ethyl alcohol. It is also applicable to the estimation of methyl alcohol. Acetaldehyde and acetal give a yellow coloration in place of the violet coloration produced by formaldehyde and methylal. T. A. H.

Detection of Methyl Alcohol. HEYWOOD SCUDDER and ROBERT B. RIGGS (*J. Amer. Chem. Soc.*, 1906, **28**, 1202—1204).—Ten c.c. of the aqueous solution (distillate) are mixed with 0.5 c.c. of sulphuric acid and 5 c.c. of saturated solution of potassium permanganate, and heated at 20—25° for two minutes, when the excess of permanganate is removed by adding a slight excess of sulphurous acid. The solution is now boiled until free from aldehyde and sulphurous acid, and then the usual ring test for formaldehyde with sulphuric acid and resorcinol is applied. The characteristic flocks formed, when applying this reaction, may be obtained also by mixing the solution with an equal volume of hydrochloric acid, then adding two drops of a 0.5 per cent. solution of resorcinol and boiling for a few minutes, but the test is less delicate than the ring test.

Leach and Lythgoe's hot copper spiral process was found to be unsatisfactory. L. DE K.

Estimation of Glycerol by Distillation. L. C. JANSSENS (*Chem. Centr.*, 1906, ii, 273; from *Seifensiederzeit.*, **33**, 286).—One side of a U-tube (c) is filled with copper turnings and the other side (a) is loosely packed with asbestos, on which is then poured as much of the slightly alkaline sample as it is capable of absorbing. Another small plug of asbestos is then introduced, and the U-tube is placed in a paraffin-bath heated at 200°. A current of steam is now passed through c, and a is connected with a small condenser and receiver, and the heating is continued until the volume of liquid in the receiver is about ten or twenty times the volume of the crude glycerol taken for analysis. The glycerol in the distillate is then calculated from the sp. gr. of the liquid, or estimated by evaporation in a vacuum, or by titration with potassium dichromate. L. DE K.

Estimation of Phenol and Thiocyanic Acid in Sewage. O. KORN (*Zeit. anal. Chem.*, 1906, **45**, 552—558).—According to Kossler and Perry, the amount of phenol in urine may be accurately estimated by treating the distillate with standard iodine in presence of alkali. The liquid is then acidified and the excess of iodine titrated as usual. Three atoms of iodine absorbed = 1 mol. of phenol. The authors now apply this principle to the estimation of the small

quantities of phenol sometimes present in sewage. Two hundred c.c. of the sample are mixed with 5 c.c. of a saturated solution of zinc acetate to remove sulphides, and the filtrate, after being rendered strongly alkaline with sodium hydroxide, is boiled down to 50 c.c. It is then transferred to a distilling flask, diluted with 100 c.c. of water, acidified with dilute sulphuric acid, and distilled until 20 c.c. are left. The distillation is then repeated twice, each time with addition of 100 c.c. of water. The first distillate is then rectified over calcium carbonate; to the residue in the retort is added the second, and finally the third fraction. The distillates are then titrated with iodine as just described.

For the estimation of thiocyanates in sewage the classified liquid should be tested by Lunge's colorimetric process with ferric chloride, using $N/10$ potassium thiocyanate as a comparison liquid.

L. DE K.

Estimation of Picric Acid. E. FEDER (*Zeit. Nahr. Genussm.*, 1906, 12, 216).—Picric acid may be estimated in aqueous solution by direct titration with $N/10$ alkali solution, using phenolphthalein as indicator, if a sufficient quantity of the latter is used. A better method consists in adding the picric acid solution to a mixture of potassium iodide with potassium iodate; the acid properties of the picric acid cause the separation of an equivalent quantity of iodine from the mixture, and this liberated iodine is titrated subsequently with thiosulphate solution, using starch solution as indicator. The change of colour from greenish-blue to pure yellow at the end of the titration is quite sharp. One c.c. of $N/10$ thiosulphate solution, or $N/10$ alkali solution, is equivalent to 0.0229 gram of picric acid. For the estimation of picric acid in solutions of its salts, it is necessary to acidify the solution with hydrochloric acid, extract the picric acid with benzene, evaporate the solvent, and dissolve the residue in water before proceeding with the titration.

W. P. S.

Detection of Traces of Resorcinol. ARTHUR CAROBBIO (*Chem. Centr.*, 1906, ii, 632; from *Boll. Chim. Farm.*, 45, 365—367).—One c.c. of an ammoniacal solution of zinc chloride is placed in a test-tube, and 1 to 2 c.c. of the ethereal solution of resorcinol is carefully poured on to the surface. A yellow ring is formed which changes to green and finally to blue. If the solution is extremely dilute, the reaction may take a very considerable time. If alcoholic hydrogen chloride is now carefully added, this will form a red layer between the ring and the ether, and on shaking, the whole ethereal layer will turn faintly red. Quinol also gives a yellow ring, which, however, changes to a brownish-red, whilst catechol and adrenaline give a ruby-red ring.

L. DE K.

Approximate Estimation of Commercial Glucose in Fruit Products. WILLIAM LYON (*J. Amer. Chem. Soc.*, 1906, 28, 998—999).—26.048 grams of the sample are dissolved, clarified, and inverted as usual, then diluted to 200 c.c. and polarised in a 20 cm. tube. If a represents the total solids; b , the polarisation in sugar degrees; x , the percentage of dextrose; and y , the percentage of sucrose and invert sugar,

then after inversion, assuming that 1 per cent. of commercial glucose causes a rotation of $+175^\circ$, and 1 per cent. of invert sugar a rotation of -0.34° at a temperature of 20° , we have: $X+y=a$, and $1.75x-0.34y=b$; therefore $x=0.34a+b/2.09$.

The solids are found, as usual, by diluting a known weight of the sample with water to a definite volume, and taking the sp. gr. of the solution.

L. DE K.

Estimation of Dextrose in Urine. ARTHUR WIESLER (*Zeit. angew. Chem.*, 1903, 19, 1547—1548).—The author prefers using the polariscope. One hundred c.c. of urine are placed in a tared flask, graduated at 100 and 110 c.c., and weighed. This gives the sp. gr., which is useful to know in case it is intended to report the sugar by weight. Five or more c.c. of alumina-cream are added, the volume is made up to 110 c.c. exactly, and the whole is well shaken and filtered. The amount of dextrose is now determined polarimetrically, as usual, by observation in a 20 cm. tube.

L. DE K.

Detection of Dextrose in Urine in Presence of Mercury. LOUIS WILLEN (*Chem. Centr.*, 1906, ii, 634; from *Schweiz. Woch. Pharm.*, 44, 394).—Bechhold's statement (this vol., ii, 129) that the Nylander sugar test is interfered with by the presence of mercury is incorrect.

L. DE K.

Estimation of Sugar in Urine by a Modification of Trommer's Method. KARL SIMROCK (*Chem. Centr.*, 1906, 11, 717; from *Munch. med. Woch.*, 53, 865).—Hein's copper solution, consisting of 2 grams of copper sulphate, 15 grams of water, 15 grams of glycerol, and 150 grams of 5 per cent. potassium hydroxide solution, is recommended as a test for sugar in urine. A previous clarification with lead acetate is not necessary. The test is not interfered with by the administration of iodine, senna, salipyrin, salol, phenacetin, and antipyrin, neither by albumen and biliary pigments, but is affected by turpentine and certain medicinal salicylic preparations, also by large quantities of uric acid and creatinine.

L. DE K.

Fermentation of Cane Molasses, and its Bearing on the Estimation of the Sugars present. GEORGE HARKER (*J. Soc. Chem. Ind.*, 1906, 25, 831—836).—The experiments carried out by the author show that the possible yield of alcohol from cane molasses, as indicated by analysis, is considerably higher than that which can be obtained by fermentation, and that this is due to the fact that the analytical figures overstate the amount of fermentable sugars actually present. The non-sugar substances present in molasses, or spent wash, exercise no harmful influence on the fermentation, and it appears probable that the substances, whatever they may be, which count as saccharose in the analysis and which are inverted by acids, but not by invertase, are decomposed by some enzyme in the yeast during the earlier stages of the fermentation.

W. P. S.

Detection of Sucrose in Presence of Lactose. A. GAWALOWSKI (*Zeit. anal. Chem.*, 1906, **45**, 620).—Leffmann has applied the sesame oil-sugar reaction to the detection of sucrose in commercial milk sugar (this vol., ii, 586). The author states that he published the same process previously (Abstr., 1899, ii, 254). L. DE K.

Optical Estimation of Mixtures of Sucrose and Raffinose. J. PIERAERTS (*Chem. Centr.*, 1906, ii, 562; from *Bull. Assoc. Chim. Sucr. Dist.*, 1906, **23**, 1261—1265).—Fifty c.c. of a solution of 10 grams of the mixed sugars in 100 c.c. of water are boiled with 10 c.c. of 20 per cent. citric acid for fifteen minutes in a reflux apparatus; the mixture is then clarified with 2 c.c. of aluminium hydroxide, made up to 100 c.c., and filtered. This solution is then examined in the polariscope at 20°, and the reading α_1 is compared with the reading α obtained from a solution of the unaltered sugar of the same strength. The amount of sucrose x , and of raffinose y in 100 c.c. of the 5 per cent. solution, can be calculated from the formulæ, $\alpha = 40 \times \frac{66.5}{100}x + 40 \times \frac{104.5}{100}y$; and $\alpha_1 = -40 \times \frac{19.84}{95}x + 40 \times \frac{53}{100}y$. P. H.

Analysis of Maple Products. ALBERT P. SY (*Chem. Centr.*, 1906, ii, 714; from *J. Franklin Inst.*, **162**, 71—72).—The malonic acid contained in these products is best estimated by precipitation with normal lead acetate, and converting the washed precipitate into lead sulphate by repeated evaporation with nitric and sulphuric acids.

L. DE K.

Determination of the "Lead Number" in Maple Syrup and Maple Sugar. A. L. WINTON and J. LEHN KREIDER (*J. Amer. Chem. Soc.*, 1906, **28**, 1204—1209).—Maple sugars and syrups are characterised by the copious precipitate they yield with basic lead acetate (Abstr., 1905, ii, 122). The authors have constructed tables showing the amount of lead precipitated by a number of samples, pure and adulterated, with other sugars ("Lead number").

The "Lead number" is determined as follows: 26.048 grams of the sample (the solution may then serve for polariscopic purposes) are weighed in a 100 c.c. flask, 25 c.c. of standard basic lead acetate are added, and the whole is diluted up to the mark and well shaken. After waiting for an hour, 10 c.c. of the filtrate are diluted to 50 c.c., a slight excess of dilute sulphuric acid is added and also 100 c.c. of alcohol. The lead sulphate is then collected, washed with alcohol, gently ignited, and weighed. Its weight $\times 0.6829$ = lead, is deducted from the amount contained in 2.5 c.c. lead solution, and the difference is the "Lead number."

The lead in the standard solution is also estimated as sulphate.

The "Lead number" of genuine maple sugars varies from 1.83 to 2.48; maple syrups give 1.21 to 1.79. L. DE K.

Inositol. G. MEILLÈRE (*J. Pharm. Chim.*, 1906, [vi], **24**, 241—246).—A method of detecting inositol in urine is described,

which depends essentially on the formation of the lead compound of inositol by the addition of basic lead acetate to the urine, previously freed from chlorides and colouring matter by successive additions of silver and lead nitrates. The inositol is liberated from the lead compound by passing hydrogen sulphide through its suspension in water. From the aqueous solution, after suitable concentration, the inositol is obtained by precipitation with alcohol, or, if necessary, with alcohol followed by ether. If the urine contains albumin, this is coagulated by boiling before adding lead nitrate, and if sugars such as dextrose are present, these are separated from the crude inositol, isolated as described above, by dissolving this in water and fractionating with copper acetate solution, the copper compound of inositol being obtained in the first fractions from which it may be regenerated by means of hydrogen sulphide.

The author identifies inositol, in preparations made in these ways, by means of the characteristic cinnabar-red residue obtained when solution of mercuric nitrate in dilute nitric acid is added to the alcohol and the mixture is evaporated to dryness at 110° to 115° , and by the initial production of an eosin-like tint and the ultimate separation of red droplets when strontium acetate is added to the colourless solution of this residue in slightly diluted acetic acid (it is insoluble in the anhydrous acid), and the solution is heated on the water-bath.

T. A. H.

Estimation of Glycogen. EDUARD PFLÜGER (*Pflüger's Archiv*, 1906, 114, 231—247).—A detailed description of the author's method is given. One hundred grams of the freshly-minced organ of a recently killed animal are boiled for at least three hours with 100 c.c. of 60 per cent. potassium hydroxide. After cooling, the mixture is diluted to 400 c.c. with water, and 800 c.c. of 96 per cent. alcohol are added; the precipitate is allowed to settle, and, after the clear liquid has been decanted on to a filter, the precipitate is washed three times in succession with 96 per cent. alcohol (containing 1 c.c. of saturated sodium chloride solution per litre), then with absolute alcohol, ether, and once more with absolute alcohol. The portion of the precipitate passing on to the filter is washed back again into the vessel containing the bulk of the precipitate and the whole dissolved in hot water. The turbid solution is made up to a known volume, filtered, and the filtrate examined in the polarimeter. The specific rotation of glycogen is $[\alpha]_D = 196.57^{\circ}$. Results of experiments are recorded showing that the rotation is strictly proportional to the concentration of the solution, and that the results agree with those obtained by inversion and titration with Fehling's solution.

W. P. S.

Estimation of Formic Acid by Potassium Permanganate. JOSEPH KLEIN (*Ber.*, 1906, 39, 2640—2641).—A claim for priority (compare Grossmann and Aufrecht, this vol., ii, 634).

A. McK.

Estimation of Volatile Acidity in Wines. SAUNIER (*Ann. Chim. anal.*, 1906, 11, 326—329).—A criticism of Hubert's process (this vol.,

ii, 635). The volatile acids should be titrated in the distillate and not be obtained by difference.
L. DE K.

Detection of Acetoacetic Acid in Urine. LUDWIG LINDEMANN (*Chem. Centr.*, 1906, ii, 717; from *Münch med. Woch.*, 53, 1019—1020).—The modified Riegler iodine test for acetoacetic acid is not interfered with by uric acid. Salicylic acid and aspirin do not give the reaction, antipyrin only when present in large quantity, and in that case a brown precipitate is obtained which dissolves gradually on shaking. Addition of sulphuric or hydrochloric acid liberates the iodine from the acetoacetic acid, but not from the uric acid or antipyrin compound. The pungent odour given off when heating urine containing acetoacetic acid with iodine is not a characteristic test for this acid.
L. DE K.

Detection of Glyoxylic Acid. ERNST SCHLOSS (*Beitr. chem. Physiol. Path.*, 1906, 8, 445—455).—See this vol., ii, 785.

Separation of *d*- and *i*-Tartaric and Racemic Acids. CHR. WINTHER (*Zeit. physikal. Chem.*, 1906, 56, 465—511).—See this vol., ii, 736.

Detection of Citrates and Tartrates [and Malates]. JAMES F. TOCHER (*Pharm. J.*, 1906, [4] 23, 87).—If to a solution of tartaric acid is added some cobalt nitrate solution followed by an excess of sodium hydroxide, the red colour disappears, but on boiling, the liquid becomes dark blue, which again vanishes on cooling. Citric acid and also malic acid give a dark blue solution, but these may be distinguished by the difference in their behaviour towards calcium chloride, and malic acid may be recognised further by the fruity odour when heated with dilute sulphuric acid and potassium dichromate. The above cobalt reaction is not given by the other ordinary organic and inorganic acids.
L. DE K.

Modification of Foerster's Fat Extraction Apparatus. ERNST PESCHECK (*Zeit. angew. Chem.* 1906, 19, 1513).—An ingenious device for fitting up the apparatus either as a Foerster or as a Soxhlet apparatus.

The latter differs from the original in so far that the siphon is placed inside the apparatus.

For details the illustration in the original should be consulted.

L. DE K.

The Method of Analysis of Milk used in the Government Laboratory for Samples referred under the Sale of Food and Drugs Acts. H. DROOP RICHMOND and E. H. MILLER (*Analyst*, 1906, 31, 317—333. Compare Thorpe, *Trans.*, 1905, 87, 206).—From the results of their investigation of this method, the authors draw the conclusions: (1) that the maceration method for fresh milks gives results which are slightly too high for the solids-not-fat, and about to the same extent that the Society of Public Analysts' method

is too low ; (2) that by the method used in the Government Laboratory, a trustworthy estimation of the composition of the original milk can be made, the results, except in cases of high butyric fermentation and other abnormal decompositions, being not more than 0.2 per cent. from the truth ; (3) that the method for the estimation of volatile acids is not a good one, and requires modification if any appreciable quantity of these acids be present ; (4) that certain small additional corrections may be made with advantage. These corrections are three in number ; the first is for the lactic acid produced ; the second is for the aldehyde taken up from the ether used, as condensation of aldehyde is shown to take place. The third correction is applied in cases where the "aldehyde number" of the evaporated milk is higher than 20, a subtraction being made from the solids-not-fat for the weight of water taken up on hydrolysis ; each degree of the aldehyde number above 20 represents a gain of 0.0018 per cent. of water. As, however, at least two forms of decomposition (a proteolytic and a butyric-propionic fermentation) were found in the examination of nineteen samples of milk, these changes requiring special corrections, the authors consider that many more experiments must be made before the analysis of sour milk can be regarded as being on a satisfactory basis.

W. P. S.

Direct Estimation of Water in Butter and other Fats. CAMILLE ASCHMAN and J. P. AREND (*Chem. Zeit.*, 1906, 30, 953).—

The process which was devised by Sjollemma is conducted by the authors as follows : Twenty to twenty-five grams of butter are introduced into a 300 c.c. distilling flask together with 75 c.c. of xylene. The flask is connected with a vertical condenser, and the distillate is collected in a graduated burette to the top of which a funnel is attached. After filling the burette with mercury up to the funnel, the distillation is started, at first rather slowly, towards the end more briskly. After distilling for about twenty-five minutes, the mercury is allowed to run from the burette, and as soon as the xylene in the funnel has become quite clear, the water is collected and measured. The results are accurate within 0.1 per cent.

L. DE K.

Java Olive Oil. KONRAD WEDEMEYER (*Zeit. Nahr. Genussm.*, 1906, 12, 210—212).—The Java olive is the seed of one of the *Sterculiaceae* ; it consists of a white kernel, a hard, brown shell and an outer, parchment-like husk, and is entirely different from the southern European olive. The oil expressed from the whole seed (kernel, shell and husk) is similar in appearance to ordinary olive oil, has a slightly rancid smell and a pleasant taste ; the yield of oil is 30.3 per cent. Its physical and chemical constants are : sp. gr. 0.9260 at 15° ; n_D 1.4654 at 40° ; iodine number, 76.6 ; saponification number, 187.9 ; Reichert-Meissl number, 0.8 ; acetyl number, 23.5 : unsaponifiable matters, 0.17 per cent. The insoluble fatty acids, which amount to 95.6 per cent., on being dried at a moderate temperature, are converted into a gum-like mass. The oil itself, when heated to a temperature of 240—245°, is also converted into an elastic, gum-like mass which is insoluble in all the usual solvents and does not harden by contact with air. Unless

precautions be taken to keep the temperature below 250° by means of cooling, sufficient heat is developed during the change to carbonise the whole mass.

W. P. S.

Owala Oil. KONRAD WEDEMEYER (*Chem. Rev. Fett. Harz. Ind.*, 1906, 13, 210—211).—This oil is obtained from the seeds of *Pentaclethra macrophylla*, a tree growing on the West Coast of Africa. The seeds vary in weight from 8 to 20 grams, and consist of about 20 per cent. of shell and 80 per cent. of kernel. The whole seeds yield 30.40 per cent. of oil, whilst the kernels alone contain 41.6 per cent. of oil; the residue left, after extracting the oil, contains 48.25 per cent. of proteid matter. The oil is pale yellow in colour, has a pleasant taste, the after-taste being slightly bitter, and an aromatic smell. After being refined, the oil could probably be classed as an edible oil. The following physical and chemical constants were obtained on the examination of the oil: Sp. gr., 0.9119 at 25° ; Reichert-Meissl number, 0.6; saponification number, 186.0; iodine number, 99.3; refractometer number, 59.2 at 40° ; acetyl number, 37.1; unsaponifiable matter, 0.54 per cent.; melting point of the fatty acids, 53.9° .

W. P. S.

Composition and Valuation of Oils Used for Gas-making Purposes. RAYMOND ROSS and JOHN P. LEATHER (*Analyst*, 1906, 31, 284—296).—The following methods were used for the valuation of an oil. For the purpose of gasifying the oil, a retort, 9 inches long, $5\frac{3}{4}$ inches wide, and $4\frac{1}{4}$ inches high, was heated in a muffle furnace to the required temperature, the gas-supply was then turned off, and 15 c.c. of the oil run into the retort during an interval of three minutes. The gas produced, after passing through a tar-bottle, was collected in a gas-holder, measured and analysed. The amount of hydrocarbons absorbed by fuming sulphuric acid was then ascertained; the number of c.c. of gas at *N.T.P.* per c.c. of oil (at 15°), multiplied by the percentage of hydrocarbons, gives a figure which the authors term the "valuation figure." A distillation test was also made on 250 c.c. of the oil, and the fractions separated at intervals of 20° . The quantity of each fraction was measured, and its sp. gr. and refractive index determined. The specific refraction was then calculated. The results of the examination of a considerable number of oils are given together with a comparison between the results obtained in the laboratory and those found by practical working on a large scale. It is seen that the method gives approximately correct results. From an investigation of the constituents of certain of the oils, the following general conclusions are arrived at: (1) the open chain compounds have the best value for gas-making purposes; (2) the presence of double bonds in the chain slightly decreases the value; (3) the presence of one or more rings decreases the value considerably; (4) the more fully hydrogenated the ring, the better its value, as compared with other ring compounds; (5) benzene rings have practically no value for "cracking" purposes.

W. P. S.

Estimation of Formaldehyde. FRANZ RUSS and B. LARSEN (*Chem. Centr.*, 1906, ii, 363; from *Mitt. Technol. Gewerb.-Mus. Wien*, [2], 16, 85—98).—A criticism of the methods at present in use for testing commercial formaldehyde. The same results are obtained by the ammonia and iodometric processes when the concentration was over 0.8 per cent., but when below this, the iodometric process gives somewhat higher results, particularly if methyl alcohol or acetone is present as an impurity. With care, the sulphite method (*Abstr.*, 1904, ii, 768) also gives good results. L. DE K.

Examination of Parts of Dead Bodies for Chloral Hydrate. H. WEFERS BETTINK and W. P. H. VAN DEN DRIESSEN MAREEUW (*Chem. Centr.*, 1906, i, 1906—1907; from *Pharm. Weekblad*, 43, 487—494).—The steam distillate of the material gave the isonitrile reaction, and, when heated at 50° with sodium hydroxide and resorcinol, gave a red coloration; both of these are reactions of chloral hydrate or chloroform. After rendering the material alkaline, the steam distillate gave a more intense isonitrile reaction than that obtained after distillation of the acidified matter, so that the substance present was probably chloral hydrate. The latter was isolated by shaking with 70 per cent. alcohol, filtering, evaporating the alcohol in a vacuum, filtering again, rendering faintly alkaline with ammonia, and shaking with ether, which gave a crystalline residue of chloral hydrate.

The methods given by Kippenberger (*Abstr.*, 1900, ii, 581) and by Arganchelsky for the estimation of chloral give divergent values. The author proposes the following method: a weighed quantity of the finely-divided material is heated for an hour at 50—60° with twice its volume of 70 per cent. alcohol, and is pressed in the cold and twice treated in the same way with 50 per cent. alcohol. When quite cold, the whole of the liquid is filtered, acidified with nitric acid, and just sufficient silver nitrate solution added to precipitate the chlorides. Any excess of silver nitrate is removed by shaking with magnesium oxide, and the precipitate formed washed with 60 per cent. alcohol. The alcoholic liquids are now boiled for five hours with potassium hydroxide free from chlorine and, on cooling, the chloride set free from the chloral estimated by acidifying with nitric acid and precipitating with silver nitrate. T. H. P.

Detection of Small Quantities of Leucine. FRITZ LIPPICH (*Ber.*, 1906, 39, 2953—2956).—See this vol., i, 813.

New Urometer; Modification of the Hypobromite Method. WILLIAM M. DEHN (*Zeit. anal. Chem.*, 1906, 45, 604—613).—A modified urometer is described which allows the careful measurement of 1 or 2 c.c. of urine, and its slow or rapid introduction into the midst of a column of hypobromite solution, and further enables some more of this reagent to be added after the nitrogen ceases to be evolved. After measuring the gas within ten minutes, a check experiment is made, using a standard solution of urea of such a strength that the volume of gas evolved shall not differ greatly from

that obtained from the urine. The urea is then found by a simple calculation.

In this process all errors due to the incomplete liberation of nitrogen from urea and conditions of measurement are eliminated. If the reading is taken after about five minutes, the minor nitrogenous constituents have not yet liberated their nitrogen, so no error can accrue from that source.

L. DE K.

Alkaloid Reactions. Berberine. C. REICHARD (*Chem. Centr.*, 1906, ii, 364; from *Pharm. Centr.-Halle*, 47, 473—478).—Berberine hydrochloride dissolves in stannous chloride with a yellow colour which is not affected by heating; if bismuth chloride is used instead, a brownish-black colour is noticed on heating. On heating with sulphuric acid, the hydrochloride turns dark green, whilst the nitrate turns dark brown. A mixture of the hydrochloride and mercurous nitrate is turned black by sulphuric acid, and then becomes yellowish-red on prolonged exposure to the air. The hydrochloride when heated with a drop of a strong solution of potassium thiocyanate becomes green. A mixture of the hydrochloride and ammonium persulphate turns black with sulphuric acid. A mixture of the hydrochloride with potassium iodate turns a graphite colour on adding a drop of hydrochloric acid; this, on adding potassium hydroxide, changes to yellow. Ammonium metavanadate and a drop of hydrochloric acid give a brown deposit changing to dark grey. If a little berberine hydrochloride is placed in a solution of α -naphthol in 40 per cent. potassium hydroxide, it turns dark reddish-brown, whilst the liquid is not affected. A mixture of the hydrochloride and α -nitroso- β -naphthol turns dark green when moistened with potassium hydroxide; the mass dissolves with a blackish-green colour in sulphuric acid. A mixture of the hydrochloride and picric acid turns dark green on adding a drop of sulphuric acid, and then turns almost black on heating. A few more tests of less importance are enumerated.

L. DE K.

Two New Reactions of Cocaine. C. REICHARD (*Chem. Centr.*, 1906, ii, 634; from *Pharm. Zeit.*, 51, 591—592. Compare Abstr., 1904, ii, 374).—If a pinch of α -naphthol is dissolved in a few drops of 40 per cent. potassium hydroxide, and a few crystals of cocaine hydrochloride are placed in the centre of the liquid, a dark blue coloration is formed, which is not affected by hydrochloric acid or ammonia. For forensic purposes, it is advisable to absorb the blue liquid in a strip of filter paper and then let it dry in the air. If a square piece of filter paper, previously dipped in tincture of Brazilwood, is moistened with water on a glass plate and then sprinkled over with a few crystals of cocaine hydrochloride, the brownish-yellow paper shows carmine-red spots; this test, however, is not characteristic for cocaine, as it is also given by other alkaloids.

L. DE K.

Colorimetric Estimation of Small Quantities of Morphine. CARL MAI and C. RATH (*Arch. Pharm.*, 1906, 244, 300—301).—A suitable quantity of this solution is evaporated in a small hemispherical glass dish on the water-bath; the residue is stirred with 1 c.c. of

Marquis' reagent (two drops of 40 per cent. formaldehyde solution mixed with 3 c.c. of sulphuric acid); and the violet liquid is transferred to a tube about 1 cm. in bore, the basin being rinsed into the tube with 4 c.c. of sulphuric acid. The amount of morphine present is estimated colorimetrically by comparison with a liquid obtained in precisely the same way from a solution containing a known quantity of morphine. Amounts of morphine as small as 0.00003 gram can be estimated in this way.

C. F. B.

Alkaloid Reactions. Quinoidine. C. REICHARD (*Chem. Centr.*, 1906, ii, 364—365; from *Pharm. Zeit.*, 51, 532—533).—Copper sulphate solution, added to quinoidine and evaporated, yields a dark green residue which turns pale green on adding solutions of methylamine hydrochloride; when again dried, and then moistened with aqueous potassium hydroxide, a dark blue colour is obtained. If to a particle of quinoidine is added a crystal of mercurous nitrate and a drop of water, a dirty, yellowish-green solution is obtained on warming, which forms on drying a similar varnish which dissolves in a drop of acetic acid with a dirty, yellow colour. Quinoidine is soluble on heating in formalin with a pale or dark green colour. If a mixture of quinoidine and picric acid is evaporated with a drop of 40 per cent. potassium hydroxide, and then moistened with a drop of strong aqueous potassium thiocyanate, a beautiful reddish-brown colour is formed. An aqueous solution of hydroxylamine hydrochloride dissolves quinoidine almost completely on warming, and leaves on evaporation a pale green residue.

L. DE K.

Glucoside Reactions. Arbutin. C. REICHARD (*Chem. Centr.*, 1906, ii, 634—635; from *Pharm. Centr.-Halle*, 47, 555—560).—A mixture of arbutin and mercurous nitrate gradually turns black when moistened with sulphuric acid. When heated with an acid solution of stannous chloride, arbutin turns first yellowish-green and then almost black. If to a solution of vanillin in sulphuric acid is added a little arbutin, the yellow solution turns brownish-red. A mixture of arbutin and ammonium molybdate is not affected by water or alkalis, but turns blue instantly on adding sulphuric acid, as also, but more slowly, with hydrochloric acid. A mixture of arbutin and α -naphthol turns dark blue on heating with a drop of hydrochloric acid. A mixture of arbutin and potassium iodate turns dark brown on adding water. When hydrochloric acid is added to arbutin mixed with potassium ferrocyanate, a dark blue liquid is obtained. A mixture of arbutin and cobalt nitrate solution turns dark brown when heated. A mixture of arbutin and potassium thiocyanate becomes yellow when moistened with sulphuric acid, and on heating gently, a characteristic odour is developed. A few more tests of less importance are given. L. DE K.

Estimation of Indigotin in Commercial Indigo and in Indigo-yielding Plants. CYRIL BERGTHEIL and RICHARD V. BRIGGS (*J. Soc. Chem. Ind.*, 1906, 25, 729—735).—The results of the investigation carried out by the authors show that fairly concordant figures may be obtained with all the usual methods employed, depending on the oxidation or reduction of sulphonated indigos, except that in

which barium chloride is used as a precipitant. The permanganate methods are more rapid in execution than the reduction or gravimetric methods, and no increase in the sharpness of the end point of the titration was noticed when applying Grossmann's modification of the permanganate process. Purification with calcium carbonate is essential to reduction methods, and one of the latter should be used in estimating indigotin in indigos containing indirubin, this constituent being then estimated separately by a special method and deducted. For all other indigos the following process gives the most trustworthy results: 0.5 gram of the finely-powdered indigo is placed in a small stoppered bottle, mixed with a few Bohemian garnets, 20 c.c. of concentrated sulphuric acid are added, and the bottle and its contents, the stopper being removed, heated in a boiling water-bath. The stopper is then replaced in the bottle, which is shaken periodically for fifteen minutes. After cooling, the contents of the bottle are transferred to a 500 c.c. flask, in which 10 c.c. of 20 per cent. barium chloride solution and sufficient sulphuric acid to precipitate all the barium have been placed previously, the mixture is made up to volume with water, and allowed to settle. A known volume of the clear supernatant liquid is now titrated with $N/50$ permanganate solution, and the result calculated on the assumption that 1 c.c. of the permanganate solution is equivalent to 0.0015 gram of indigotin.

The "persulphuric acid method" (Trans., 1904, 85, 877) for determining the amount of indigotin obtainable from an extract of indigo plant is shown to be trustworthy. W. P. S.

Analysis of Indigo. W. POPPLEWELL BLOXAM (*J. Soc. Chem. Ind.*, 1906, 25, 735—744. Compare Trans., 1905, 87, 974).—The following conditions are given under which indigotin may be separated quantitatively as potassium indigotintetrasulphonate, by means of potassium acetate, from solutions of the sulphonates of either pure indigotin or of crude indigo. In the case of pure indigotin, 1 gram of the sample, dried previously at 110° , is heated in a water-oven for half an hour with 2 or 3 grams of clean sand and 5 c.c. of fuming sulphuric acid (20 per cent. SO_3). After cooling, the mixture is diluted to 500 c.c. with water; 100 c.c. of this solution are placed in a capacious conical beaker and 100 c.c. of a 45 per cent. potassium acetate solution are run in; the contents of the beaker are next heated until complete solution of the precipitate has taken place, and then cooled by placing the beaker in a mixture of ice and water for one hour. The tetrasulphonate separates as a fine-grained, crystalline precipitate, and this is collected on a filter moistened with a solution prepared by adding 5 c.c. of glacial acetic acid to 200 c.c. of 45 per cent. potassium acetate solution, and diluting the mixture with 400 c.c. of water. The precipitate is then dissolved off the filter with hot water, the solution made up to 200 c.c. with water, and portions of it titrated with potassium permanganate or titanium trichloride solutions. If the former solution is used, 20 c.c. of the tetrasulphonate solution are diluted with 80 c.c. of water, 0.5 c.c. of sulphuric acid is added, and a 0.1 per cent. potassium permanganate solution run in until the addition of a drop no longer produces a cloud in the pure yellow liquid. Pure

indigotin would require in these circumstances 9.0 c.c. of permanganate, and percentages are calculated from this standard. When the titration is performed with titanium trichloride solution, 25 c.c. of the tetrasulphonate solution are treated with 1.5 c.c. of a 20 per cent. disodium tartrate solution, and the mixture titrated at a boiling temperature in an atmosphere of carbon dioxide.

The process described above may be applied to crude indigo, but with one or two modifications. Fuming sulphuric acid containing 25—26 per cent. of SO_3 must be used for the sulphonation, the precipitate of the tetrasulphonate is washed on the filter with the acidified potassium acetate solution until the brown colour of the washings changes to faint blue, and the filtrate is passed through a second filter to collect any precipitate which may have escaped the first filtration.

W. P. S.

Analysis of Indigo. CHRISTOPHER RAWSON (*J. Soc. Dyers Colourists*, 1906, 22, 306—307).—The author criticises Bloxam's statement that the permanganate method is untrustworthy (compare *Trans.*, 1904, 85, 870; 1905, 87, 975, and *J. Soc. Chem. Ind.*, 25, 735), and considers that the erroneous results obtained by Bloxam were due to his not having followed the exact conditions of the process. W. P. S.

Estimation of Digestible Proteids in Foods. ALBERT STUTZER (*J. Landw.*, 1906, 54, 235—256).—In separating the proteids, the substance (1 gram) is heated with 100 c.c. of water, treated first with 20 c.c. of 10 per cent. copper sulphate solution, and after some time with 20 c.c. of 2.5 per cent. sodium hydroxide solution. It is subsequently filtered and washed, and the nitrogen estimated in the usual manner.

The digestible proteids are determined by digesting the substance (2 grams) with 500 c.c. of gastric juice (prepared as described in former papers) for forty-eight hours at blood temperature, the acidity of the liquid being gradually raised to 1 per cent. hydrochloric acid.

N. H. J. M.

Further Simplification of the Method of Estimating the Pepsin-soluble Nitrogen of Foods. ALBERT STUTZER, H. WANG-NICK, and W. ROTHE (*J. Landw.*, 1906, 54, 265—272).—It is preferable to employ gastric juice twice as concentrated as that used hitherto. The method of preparation is as follows: the inner mucous membranes of at least six fresh pigs' stomachs are cut up and, after being frequently shaken with 0.2 per cent. hydrochloric acid (2.5 litres per stomach), kept in a cool place for twenty-four hours. It is then filtered successively through flannel and filter-paper. Chloroform is added until a portion remains undissolved. N. H. J. M.

General and Physical Chemistry.

Wave-length Tables of the Spectra of the Elements and Compounds. SIR HENRY E. ROSCOE, W. MARSHALL WATTS, SIR NORMAN LOCKYER, SIR JAMES DEWAR, GEORGE D. LIVEING, ARTHUR SCHUSTER, W. NOEL HARTLEY, WOLCOTT GIBBS, SIR WILLIAM DE W. ABNEY, and WALTER E. ADENEY (*Brit. Assoc. Rep.*, 1905, 105).—Wave-length tables of the spectrum of neon and of the two spectra of krypton and xenon obtained respectively with and without Leyden jar and spark gap. G. T. M.

The Spectra of Arsenic and the Spectrum of Antimony in a Geissler Tube. JOSEPH HERPERTZ (*Chem. Centr.*, 1906, ii, 1105; from *Zeit. wiss. Photogr. Photophys. Photochem.*, 1906, 4, 185—197).—The spectra of arsenic produced by means of the electric arc and by sparks have been measured and recorded in tabular form. To obtain the spectrum of antimony, the trioxide was heated in a hard glass tube by means of two Bunsen burners. P. H.

Band Spectrum of Boron. GEORG KÜHNE (*Chem. Centr.*, 1906, ii, 1105; from *Zeit. wiss. Photogr. Photophys. Photochem.*, 1906, 4, 173—184).—By means of a Rowland concave grating of radius of curvature 6.6 m., the author has photographed the spectrum produced by passing sparks between carbon poles covered with a layer of boric acid by dipping them into the fused substance. The wave-lengths have been tabulated. P. H.

Spectrum of a New Gas contained in the Atmosphere. RUDOLF SCHMIDT (*Chem. Centr.*, 1906, ii, 849—850; from *Ber. Deut. physikal. Ges.*, 1906, 4, 277—282).—By fractionally distilling liquid air and condensing the distillates in wood charcoal, cooled by means of liquid air, a fraction giving an abnormal ultra-violet spectrum was obtained. The lines described by Baly as common to krypton and xenon did not appear intensified or singly, although the majority of the xenon lines, with the exception of the brightest ones, could be identified. On the other hand, the brightest lines in this spectrum were those which were faintest in Baly's spectrum; as, moreover, some entirely new lines were observed, the conclusion is drawn that this is a new gas of high atomic weight and that xenon is a mixture. P. H.

Fluorescence and Magnetic Rotation Spectra of Sodium Vapour and their Analysis. ROBERT W. WOOD (*Phil. Mag.*, 1906, [vi], 12, 499—524).—The absorption spectrum of sodium vapour was investigated in the portion between wave-lengths 4600 and 5700, and was photographed with a 12-foot concave grating. The part specified consists of about 1500 lines and is profoundly modified by the presence of inert gases. Few of the lines have any relation with the fluorescent and magnetic rotation spectra, but it is noteworthy

that those concerned, however, are those which are affected by an inert gas. The magnetic rotation spectrum was photographed by aid of the grating, and also by a wide dispersion 3-prism spectrograph. About 60 lines were obtained with very varying intensity. The fluorescent spectrum for white light excitation is also a bright line spectrum, the lines coinciding with those of the magnetic spectrum, but being generally broader. For the analysis of these spectra, the fluorescent spectra for monochromatic excitation were examined. That obtained by excitation by the cadmium line 4800 was found to consist of a series of 16 lines spaced at regular wave-length differences (approx. 38), but with three of these lines missing. One of the lines coincides with the silver line 5207, and excitation by this line gave the series complete. The green cadmium line 5086 gave eleven pairs of lines regularly spaced, one series of which coincides with the magnetic spectrum—the difference as before is about 38. For the second series the author is unable to account, and it is the only case recorded of a spectrum of doublets produced by monochromatic stimulation. The spectra produced by excitation by the zinc arc, bismuth arc, copper, lead, helium, barium, and sodium were also examined, photographs are reproduced, and a chart is also given. That from zinc excitation is somewhat complex, and although regularity probably exists, it has not been sufficiently carefully studied. Although the operative bismuth 4724 is very close to the zinc line 4722, yet the spectra produced are quite different, the bismuth excitation giving a spectrum with regularly spaced lines in the violet and a complex assortment in the yellowish-green, the intervening space being devoid of lines. The line 5001 of lead gave a marked series coincident with one of the series of the magnetic spectrum. Line 5015 of helium gives a regular series of lines, as does line 4713. The latter line is identical with a line in the spectrum excited by zinc 4680, and there is perfect agreement in position between the fluorescent lines in both cases. Two lithium lines were operative, namely, 4601 and 4971; of these the first is the shortest monochromatic stimulant found, and gives a series in the violet and many lines in the yellowish-green. The second line also gives a series in the green, coincident with a magnetic series. Sodium light gives resonance radiation. Cathode rays excite fluorescence similar to that of white light. It was found also that where the cathode rays entered and left the vapour, spots of light respectively green and yellow were produced, the intervening space being dark, but these separate lights have not been investigated. In the composite spectra, built up from the several monochromatic ones, many more lines are found than in the white light spectrum, and by aid of the monochromatic spectra the magnetic spectrum is divided into six series of lines with difference of approximately 38 (only four lying outside limits 37.5 and 39.5). A few lines are not placed. The theoretical discussion is deferred (see also Abstr., 1905, ii, 783; this vol., ii, 319).

L. M. J.

Theory of Optical Activity. II. CHR. WINTHER (*Zeit. physikal. Chem.*, 1906, **56**, 703—718. Compare this vol., ii, 320).—Other cases where $\Delta[\alpha] = k \cdot \Delta v$ are furnished by solutions of camphor and *l*-tur-

pentine oil in various solvents. Further, many examples of pure active substances are found to which the formula $\Delta[\alpha] = k_1 \cdot \Delta T / TT_1 + k_2 \cdot \Delta v$ is applicable, and the values of k_1 and k_2 are given for each case.

The observations previously made (see Abstr., 1904, ii, 4) in connexion with rotation dispersion are discussed afresh in the light of the theory. It is probable that in solutions where no combination takes place between solvent and solute (which according to the theory would be shown by equality of the constants for the solution with those for the pure solute) the solution dispersion coefficients must be equal to the rational dispersion coefficients.

J. C. P.

Rotatory Power of Coloured Solutions. I. Action of Alkaline Copper Solutions on the Rotation of Sugars, Higher Alcohols, and Hydroxy-acids. HERMANN GROSSMANN (*Zeit. Ver. deut. Zuckerind.*, 1906, 610, 1024—1035).—The author has investigated the influence of alkaline copper solutions on the rotations of dextrose, lævulose, sucrose, mannitol, rhamnose, isosaccharin, tartaric and quinic acids, and asparagine. By using Landolt's pale blue light-filter, light of wave-length $488.5 \mu\mu$ (*hb*) was obtained.

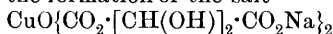
The action of alkaline copper solutions on the rotations of hydroxy- and amino-compounds is extraordinarily great, the rotations being, in some cases, reversed in sign. Copper must hence be classed with those elements which, on account of a marked tendency to form complexes, act strongly on the rotation; this property is possibly connected with the high absorptive powers of solutions of this element in the visible and ultra-violet portions of the spectrum.

With dextrose, lævulose, sucrose, and rhamnose, the rotation is changed in sign; with the other compounds mentioned, the rotation is increased in magnitude.

In the case of dextrose, the greatest change obtained in the value of $[\alpha]_{hb}$ by the presence of copper sulphate was from $+78.0^\circ$ to -375° ; with lævulose, from -134.5° to $+1423^\circ$; with sucrose, from $+101.2^\circ$ to -111.3° ; with mannitol, from a small negative value to -920° ; with rhamnose, from $+12^\circ$ to -551° .

In the case of tartaric acid, the maximum change in the value of $[\alpha]_{hb}$ produced by adding copper sulphate to the alkaline solution was from $+72.0^\circ$ to $+1327^\circ$, this maximum occurring in a *N*/10 solution of the acid when from 3—4 mols. of sodium hydroxide and 1 atom of copper were present per mol. of acid. The salt $\text{Cu} \begin{smallmatrix} \text{C}(\text{OH}) \cdot \text{CO}_2\text{Na} \\ \text{C}(\text{OH}) \cdot \text{CO}_2\text{Na} \end{smallmatrix}$, to

which the increased dextrorotation is due, only exists in presence of excess of sodium hydroxide. When the dilution is great or when free sodium hydroxide is absent, there appears a lævorotatory phase, which probably depends on the formation of the salt



(compare Kahlenberg, Abstr., 1896, ii, 6); this then undergoes hydrolysis, the rotation of normal sodium tartrate being obtained. The value of $[\alpha]_{hb}$ for Fehling's solution varies from $+361.6^\circ$ for a dilution of 1:5 to $+411.1^\circ$ for a dilution of 1:40. The complexes formed by ammonia with copper tartrate differ from those given by sodium or potassium hydroxide in that the copper occurs in the cation of the

compound, $\text{Cu}(\text{NH}_3)_4\text{C}_4\text{H}_4\text{O}_6$, formed. The $[\alpha]_{hb}$ of an ammoniacal copper tartrate solution, $+66.6^\circ$, was found to be increased to $+732^\circ$ by the addition of sodium hydroxide, the transference of copper from the complex cation to the complex anion being hence clearly indicated.

The value of $[\alpha]_{hb}$ for quinic acid, -61.0° , is changed to $+410^\circ$ by the addition of alkaline copper sulphate solution; with *isosaccharin*, the greatest change is from $+81.2^\circ$ to $+473^\circ$, and with asparagine, a change from -14° to -160° was observed.

The addition of alkaline chromium chloride solution increases considerably the rotation of quinic acid, without changing its sign, whilst with mannitol, the rotation is altered in sign and greatly increased.

T. H. P.

Ultramicroscopic Studies. II. Characterisation of Inorganic Colloids. WILHELM BILTZ and W. GEIBEL (*Chem. Centr.*, 1906, ii, 851—852; from *Nachr. K. Ges. Wiss. Göttingen*, 1906, 141—156. Compare Abstr., 1904, i, 976).—An account of the optical appearance of colloidal solutions of the hydroxides of aluminium, chromium, iron, silicon, vanadium, and zirconium, as well as of prussian, tungsten, and molybdenum blues, of arsenic and antimony sulphides, and of gold. A solution of cerium ammonium nitrate in glycerol remains clear on addition of ammonia, but on addition of water to the mixture cerium hydroxide is gradually precipitated.

P. H.

Coloration of Didymium Glass by Radium Chloride. CHARLES BASKERVILLE (*J. Amer. Chem. Soc.*, 1906, 28, 1511).—About 0.6 gram of radium chloride, of 7000 activity, was sealed in a small, colourless tube composed of didymium glass containing manganese, and was left for six months. The glass became pink but exhibited no change in its absorption spectrum, and no electrical or sparking effects were observed on opening the tube.

E. G.

Radioactivity [of the Thermal Waters of S. Giuliano]. ANGELO BATTELLI, A. OCCHIALINI, and S. CHELLA (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 262—271).—The water of the thermal springs of S. Giuliano in Tuscany exhibit radioactivity caused by the presence of a substance giving an emanation similar in character to that of radium but distinguished from the latter by its duration and by the duration of the radioactivity it induces in metals. The values of $1/\lambda$ for radium and for the gases of S. Giuliano are as follows:

	For induced radioactivity	For the emanation
Radium	41	5 days 13 hours.
Gas of S. Giuliano	54	8 „ 15 „

The emanation is to be submitted to spectroscopic examination.

T. H. P.

Comparative Observations on the Evolution of Gas from the Cathode in Helium and Argon. CLARENCE A. SKINNER (*Phil. Mag.*, 1906, [vi], 12, 481—488).—When a glow current is passed

through a vacuum tube containing helium, hydrogen is given off from a metallic cathode and nitrogen from a carbon cathode during the first few minutes of the current. In an atmosphere of hydrogen with metallic electrodes, or of nitrogen with carbon electrodes, no increase of pressure occurs. Further observations have been made with aluminium and magnesium electrodes in tubes containing argon and helium. In all cases the increase of pressure was at first proportional to the current and was independent of the metal or the gas employed, and the author draws the conclusion that the negative results in hydrogen and nitrogen are due to the absorption by the anode of these gases at a rate determined by Faraday's law.

L. M. J.

Dissociation of Matter under the Influence of Light and Heat. GUSTAVE LE BON (*Compt. rend.*, 1906, 143, 647—649).—In view of a recent communication by Ramsay and Spencer (this vol., ii, 715) the author states that the conclusion drawn from his researches on the dissociating action of light on matter is that light dissociates matter, and if sufficiently intense to heat the substance submitted to its action, it expels a small quantity of the radioactive elements which all substances contain by reason of their spontaneous dissociation. Thus a charged electroscope surrounded by a thin metallic cylinder is partially discharged when exposed to the sun in summer, but the discharge is not complete until the metallic cylinder is replaced by another; and a similar partial discharge occurs if the charged electroscope surrounded by the metal cylinder is placed in the dark and a few centimetres distant from a body at a temperature of 400—500°, a discharge equivalent to 1/100 volt occurs in three to four minutes, and this can be repeated several times, after which the metal becomes inert and does not regain its power to discharge the electroscope until several weeks.

M. A. W.

Specific Inductive Capacity of Solutions of the Oleates of the Heavy Metals. LOUIS KAHLENBERG and ROLAND B. ANTHONY (*J. Chim. phys.*, 1906, 4, 358—364).—The dielectric constant of concentrated solutions of the oleates of magnesium, zinc, aluminium, nickel, cobalt, iron, and cadmium in benzene, carbon tetrachloride, chloroform, pyridine, carbon disulphide, nitrobenzene, hexonitrile, cotton-seed oil, and petroleum has been measured by a modification of Drude's method. In general, the specific inductive capacity of the solvent is diminished by the addition of the metallic oleates. The influence is not of an additive nature, and the special character of the metal present in the solution has no measurable effect on the values obtained for the dielectric constant.

H. M. D.

Oxide Theory of the Hydrogen-Oxygen Cell. RICHARD LORENZ and HANS HAUSER (*Zeit. anorg. Chem.*, 1906, 51, 81—95).—From the values obtained for the dissociation of water vapour at high temperatures, Nernst and Haber have recently estimated the *E.M.F.* of the hydrogen-oxygen cell at 1.23 volts, whilst the values actually obtained with platinum electrodes are lower, commencing at 1.08 volts

and increasing slowly to about 1.17 volts. No satisfactory explanation of these results has been obtained.

The authors have measured the *E.M.F.* of cells with electrodes of platinum and other metals, as well as of carbon, at room temperature and at 30°, sulphuric acid, sodium hydroxide, and sodium sulphate being employed as electrolytes. If what is being measured is the formation of water from gaseous hydrogen and oxygen, the *E.M.F.* should in each case be the same, but it was found that no two cells gave the same value. It was noticed that in several of the cells containing alkali, and in some of the sodium sulphate cells, the anode became oxidised, and it is therefore suggested that in all cases the *E.M.F.* at an oxygen electrode is determined by the formation of an oxide. In support of this view, it was found that the *E.M.F.*'s of the oxides of cadmium, copper, silver, iron, and nickel were identical with those of the respective metals when measured under the same conditions. Neither of the oxides of platinum gave results so high as 1.17 volts, but the potential of the hydrated dioxide is such as to account for the value formerly given for the *E.M.F.* of the hydrogen-oxygen cell, 1.08 volts. It was, however, observed that whilst platinum electrodes which had been washed several times with acid did not, even after a long time, show a higher value than -1.08 volts; a freshly platinised electrode gave a considerably higher potential. As this result cannot be due to either of the known oxides, it is suggested that a still higher oxide is formed at a freshly platinised surface. G. S.

Amalgam Potentials. A. SUCHENI (*Zeit. Elektrochem.*, 1906, 12, 726—732).—The *E.M.F.* of the combination, thallium amalgam | solution of thallos chloride in potassium chloride | calomel electrode, was measured for the complete series of amalgams of thallium. The values (at 37°) increase quite regularly from almost zero with pure mercury to 0.83 volt at 49.6 per cent. thallium and then remain constant. Measurements at 0° and -80° gave similar curves, the constant value was reached at 33 per cent. at 0°. The results are in accordance with the view that the amalgams containing more than 33 per cent. of thallium consist of an aggregate of crystals of thallium and of the compound TlHg_2 when they are completely solid, and of crystals of thallium and a saturated solution of thallium in the compound TlHg_2 when they are partly liquid. The amalgams with less than 33 per cent. of thallium must all be regarded as liquid or solid solutions of mercury in the compound TlHg_2 . That mercury is not present as an independent phase was proved by touching the solid amalgam (at -80°) with solid mercury when the *E.M.F.* at once fell to that of mercury. T. E.

Silver Titration Voltameter. WLADIMIR KISTIAKOWSKY (*Zeit. Elektrochem.*, 1906, 12, 713—715).—The instrument is suitable for the measurement of currents up to 0.2 ampere flowing for one hour at most. It consists of a glass tube 18—22 cm. long, 3.5 cm. diameter at the upper end, and 1 cm. at the lower end. The lower electrode is a disc of silver connected to a wire which is fused through a glass bead. This bead closes a piece of rubber tubing which is slipped over the lower end of the glass tube. By pinching the rubber tubing the

solution can be drawn off. The upper electrode (cathode) consists of copper gauze immersed in a solution of copper nitrate contained in a small porous pot. The remainder of the tube is filled with a 10 per cent. solution of potassium nitrate. At the end of a measurement the solution is run off and the silver which has dissolved is titrated by Volhard's method.

The results are correct to 0.1 per cent.

T. E.

Electrical Conductivities of Potassium Chloride, Bromide, and Iodide in Ethyl and Methyl Alcohols. DAVID STENQUIST (*Arkiv Kem. Min. Geol.*, 1906, 2, No. 25, 1—8).—The author's measurements lead to the following values for the equivalent conductivity Λ and the temperature coefficient C ; the concentration being in each case 0.001 gram-equivalent per litre.

Potassium iodide $\Lambda = 38.5$, $C = 0.0271$ in ethyl alcohol; $\Lambda = 88.7$, $C = 0.0188$ in methyl alcohol. Potassium bromide, $\Lambda = 36.0$, $C = 0.0264$ in ethyl alcohol; $\Lambda = 83.0$, $C = 0.0159$ in methyl alcohol. Potassium chloride, $\Lambda = 34.5$, $C = 0.0292$ in ethyl alcohol; $\Lambda = 81.0$, $C = 0.0130$ in methyl alcohol.

T. H. P.

Relation between Electrolytic Dissociation and Dielectric Constant. EMIL BAUR (*Zeit. Elektrochem.*, 1906, 12, 725—726).—In a former paper (this vol., ii, 144) the author attempted to show that if two solutions of a binary electrolyte in different solvents are in equilibrium with each other, the concentrations of the ions in the two solutions will be in the ratio of the cubes of the dielectric constants of the solvents. An experimental confirmation of this view is furnished by Walden's results (this vol., ii, 149 and 527). He found that the concentrations at which tetraethylammonium iodide is equally dissociated in different solvents are in the same ratio as the cubes of the dielectric constants of the solvents, and further, that saturated solutions of tetraethylammonium iodide in different solvents are all equally dissociated. Since saturated solutions are in equilibrium with each other, this confirms the author's hypothesis (for saturated solutions).

T. E.

Periodical Phenomena in Electrolysis. ALFRED THIEL and A. WINDELSCHMIDT (*Zeit. Elektrochem.*, 1906, 12, 737).—During the deposition of nickel from solutions containing ammonia or oxalic acid, nickel peroxide is formed and redissolved at the anode periodically. The current and voltage undergo corresponding periodic variations.

T. E.

Relative Migration Velocities of the Ions of Silver Nitrate in Water, Methyl Alcohol, Ethyl Alcohol, and Acetone, and in Binary Mixtures of these Solvents, together with the Conductivity of such Solutions. HARRY C. JONES and CHARLES A. ROUILLER (*Amer. Chem. J.*, 1906, 36, 427—487).—After a brief historical review of previous work in this field, an account is given of experiments carried out in continuation of the investigation of Jones and Bassett (*Abstr.*, 1905, ii, 8).

The conductivity of silver nitrate and the transport number of its anion in binary mixtures of water, methyl alcohol, ethyl alcohol, and acetone have been determined at 0° and 25°, all the measurements being made with 0.02 *N* solutions. The results are tabulated and plotted as curves, and are of the same general nature as those obtained previously with calcium nitrate. The observation is confirmed that, as a rule, the velocity of the slower ion increases with rise of temperature. This is not so, however, in solutions in pure methyl alcohol, in a mixture of methyl alcohol and water containing 75 per cent. of the former, or in mixtures of methyl alcohol and acetone. The relative migration velocities are influenced largely by the nature of the solvent, and this is probably due to varying degrees of combination of the solvent with one of the ions. E. G.

Theory of Amphoteric Electrolytes. HARALD LUNDÉN (*Arkiv Kem. Min. Geol.*, 1906, 2, No. 18, 1—6. Compare this vol., ii, 265).—The author points out that the conclusion drawn by Winkelblech (*Abstr.*, 1901, ii, 370) that the degree of hydrolysis (x) of an amphoteric electrolyte can be calculated by means of the equation, $k_s k_b / K_w = [(1 - x)/x]^2$, is erroneous.

The author's calculations (*Arkiv Kem. Min. Geol.*, 1906, 2, No. 11, and *loc. cit.*) of the degree of hydrolysis of the internal salt and of the heat of the reaction, amphoteric electrolyte \rightleftharpoons internal salt, are also erroneous.

It is shown that, with amphoteric electrolytes, the conductivity cannot be small, and the experimentally determined dissociation constants, k_s and k_b , at the same time large (compare Walker, *Abstr.*, 1904, ii, 309; 1905, ii, 138). These constants, determined by experiment, are not, however, the true constants, and the assumption that the latter are large and the conductivity small is not in disaccord with the equations derived by the author.

With an amphoteric electrolyte of the type ROH, internal salts cannot occur, and it may be assumed that the true salts of the form RO·R are approximately completely dissociated in dilute solution. In this case, simultaneous existence of a low conductivity and high dissociation constants is not possible. T. H. P.

Conditions of Equilibrium of an Associating Amphoteric Electrolyte in the presence of any number of Non-amphoteric Electrolytes. T. BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1906, 10, 524—582).—The theoretical conditions of equilibrium are investigated for the following systems: (A) An associating or polymerising amphoteric electrolyte (termed ampholyte), the ions of which are all univalent in the absence of other electrolytes. (B) An associating ampholyte of univalent ions in the presence of any number of non-amphoteric electrolytes of univalent ions. (C) Two associating ampholytes of univalent ions in the presence of non-amphoteric electrolytes of univalent ions. (D) An associating ampholyte of bivalent and univalent ions in the presence of electrolytes of univalent ions. (E) The similar system, but with electrolytes of bivalent and univalent

ions. In systems *A*, *B*, and *E* it is deduced that the sum of the ratios of the active masses of the dissociated basic ampholates to the active masses of the dissociated acid ampholates varies as the square of the hydron concentration. The results also indicate an alternative explanation for the relation between the precipitating power of a salt for colloids and the valency of its ions (this vol., ii, 841). The connexion between this investigation and the ion-proteid hypothesis is discussed, and the views are advanced that "ion-proteids" are in reality amphi-salts of the proteins; that non-dissociable compounds of protein with non-amphoteric ions are amphi-salts dissociating as acids and bases; that the influence of electrolytes on the reactions of tissues may be referred mainly to alterations in the ratio of basic to acid ampholates and to formation of amphi-salts. L. M. J.

Magnetic and Optical Investigations on certain Magnetic Colloids. OSCARRE SCARPA (*Nuovo Cim.*, 1906, [v], 11, 80—113 and 162—185).—After giving a *résumé* of the various views published concerning the colloidal state, the author describes his experiments, the results of which are briefly as follows.

All colloids, whether solid or suspended in water, are strongly paramagnetic and also often ferromagnetic, whilst the corresponding solutions are generally diamagnetic owing to the preponderating action of the water. The specific magnetism is very great for Bredig's colloids and, on comparing the values obtained with those given by Meyer (Abstr., 1900, ii, 7) for solid oxides, indications are obtained of the existence in these colloids of metallic granules; this view is supported by the observation that the colour of colloidal solutions of iron gradually changes from a greenish-yellowish-brown to reddish-yellow, probably owing to slow oxidation. With Bredig's colloids (iron, nickel, and cobalt) there is a marked dependence of the specific magnetism on the intensity of the inducing field, a phenomenon which is uncertain with chromium and manganese, and absent in the case of vanadium; residual magnetism, and hence hysteresis, occurs in the cases of iron and nickel and, possibly, in cobalt. Variation of the susceptibility, with change of intensity of field from 4500 to 5500 units does not occur with solutions of ferric acetate or of basic acetates of iron, and is doubtful with oxides of iron prepared according to Graham; with two colloidal ferric oxides, prepared by the method given by Péan de Saint-Gilles, and especially with acetates of iron modified by heat under high pressure, the specific magnetism diminishes as the field increases in intensity.

Bredig's colloids all exhibit positive magnetic rotation, that is, rotation in the same sense as that of water, although ferrous and ferric salts have a negative, and salts of nickel, cobalt and manganese, a positive rotation. The colloids hence rotate like their respective metals, a fact which may be taken to indicate that colloidal solutions of iron contain true metallic granules, the action of which would preponderate over that of the granules of oxide undoubtedly present. Chemical colloids of oxide of iron always exhibit negative magnetic rotation, which is very weak in Graham's oxides and their analogues (hydrolysed and basic acetates), greater for the colloids of Saint-Gilles, and still greater

with the acetates modified by the action of heat and pressure; with the last compounds it is 550 times as great as that of water.

The absorption spectra of all colloids exhibit an absorption increasing rapidly from the yellowish-green to the violet, and a few exert a weak absorption diminishing from the extreme red to the orange; in general they seem to follow Rayleigh's laws for the passage of light in media rendered turbid by suspended particles. No bands of absorptive selection were observed in the visible spectrum.

Bredig's colloids exhibit electrical conductivity somewhat greater than that of the distilled water in which they are formed, but no law could be found connecting the conductivity and the concentration of the solution; with these colloids, spontaneous coagulation in the electrolytic cell does not alter the conductivity by more than 2 per cent. Chemical colloids, which were purified by dialysing them for 12 months, and in which no traces of extraneous substances could be detected, exhibited extremely small conductivities of the same order as those of Bredig's colloids. By dilution of either Bredig's colloids or purified chemical colloids with distilled water, the conductivity is shown to be an additive property.

In the case of Bredig's colloids and some of the purified chemical ones, the density differs insensibly, or but slightly, from that of water; with the others, the presence of impurities introduces complications. The density of colloids is also additive with respect to the dilution.

All Bredig's colloids and all the oxides of iron prepared chemically, with the exception of one colloidal ferric hydroxide, are electropositive, that is, transport takes place in the direction of the current.

The paper concludes with descriptions of the preparation, general characters, and methods of analysis of the different colloids.

T. H. P.

New Low Temperature Phenomena. SIR JAMES DEWAR (*Proc. Roy. Inst.*, 1906, 18, 177—192).—The absorptive power of charcoal at low temperatures (see Abstr., 1904, ii, 652, 728, 729) is further demonstrated by the following experiments. Air which has been passed through a tube containing charcoal and kept at -78° is entirely freed from carbon dioxide, the complete absorption continuing until the charcoal has absorbed about 1 per cent. of its weight of carbon dioxide. On the other hand, air passed through a tube cooled to -78° , but containing no charcoal, remains fully charged with carbon dioxide.

The power of charcoal to absorb hydrocarbons is shown by passing a current of coal gas through a bulb charged with charcoal and kept at -78° , when the issuing gas burns with a non-luminous flame.

By the use of a bulb of oxygen, connected with a tube containing phosphorus and another containing charcoal, the author has shown that perfectly dry oxygen combines with phosphorus below 1 mm. pressure.

J. C. P.

Abnormal Depression of the Transition Temperature in the Case of Mixed Crystals. H. E. BOEKE (*Zeit. physikal. Chem.*, 1906, 56, 686—688).—The temperature of transition of γ - into

δ -sodium molybdate is lowered to an abnormal extent by small quantities of sodium sulphate. No explanation can so far be suggested for this marked discrepancy between observation and theory.

J. C. P.

Vaporisation of Solid Substances at the Ordinary Temperature. II. CONSTANTIN ZENGELIS (*Zeit. physikal. Chem.*, 1906, 57, 90—109. Compare Abstr., 1905, ii, 143).—The earlier observations have been extended, and the substances found to volatilise at the ordinary temperature include many peroxides, hydroxides, sulphides, halides, nitrates, carbonates, sulphates, phosphates, chlorates, and chromates. The power of absorbing the vapours seems to be specially characteristic of silver (see *loc. cit.*), and is attributed to the resistance offered by this metal to the oxidising action of the air, and to the fact that silver acts as a comparatively strong reducer. Experiments are described indicating that silver is a more powerful reducer than has generally been supposed. Thus, when a dilute ferric chloride solution is heated for two hours at 80° with silver leaf or powder, 48 per cent. of the ferric salt is reduced to ferrous salt; acidified dichromate also is reduced by prolonged heating with silver leaf; silver reduces solid copper sulphate to sulphide at temperatures below 150°.

It is noteworthy that when silver leaf is placed in dry contact with one of the foregoing substances which are volatile at the ordinary temperature, the silver is attacked only at points which are not in contact with the other substance. It is therefore the vapours of these substances which act on the silver, and it is thought probable that in their very attenuated condition they have in some way undergone dissociation. It is considered that the phenomena of radioactivity lend support to this hypothesis of a dissociation.

J. C. P.

Simple Toluene Regulator and Shaking Machine for Thermostats. HARALD LUNDÉN and WM. TATE (*Medd. k. Vetensk. Akad. Nobelinstitut*, 1906, 1, No. 5, 1—4).—The regulator is a simplified form of that described by Dony-Hénault (Abstr., 1905, ii, 142). The vertical tube from the regulator bulb is bent twice on itself so as to form a system of three parallel tubes. The descending tube is of larger diameter than the ascending tubes, the lower half of the reservoir so formed and the length of tube from this to the mercury in the ordinary U-limb being filled with calcium chloride solution.

For a description of the shaking machine the original must be consulted.

H. M. D.

Action of the Alkali and Alkali-earth Metals on a Molecule of Water. ROBERT DE FORCRAND (*Ann. Chim. Phys.*, 1906, [viii], 9, 234—241).—Representing by A and B the thermo-chemical equivalents of the equations $\text{H}_2\text{O (solid)} + \text{M (solid)} = \text{MOH (solid)} + \text{H (gas)}$, and $\text{MOH (solid)} + \text{M (solid)} = \text{M}_2\text{O (solid)} + \text{H (gas)}$, respectively, in which M represents Li, Na, K, Rb, Cs, Ca/2, Sr/2, Ba/2, Mg/2, or Zn/2, the metals can be divided into two series; in the first series comprising Na, K, Rb, and Cs, the values for $A + B$ increase, and the values for $A - B$ decrease with the atomic weights of the metals; further, the

values of A increase regularly with the atomic weight, whilst the values of B are negative and also increase with the atomic weight. The second series comprises the alkali-earth metals and lithium, and for these metals the values of $A + B$ decrease, whilst the values of $A - B$ increase slightly as the atomic weight of the metal increases; and the values of A and B , which are positive, diminish as the atomic weight of the metal increases.

M. A. W.

Azo-colouring Matters; Heat of Combustion and Constitutional Formula. PAUL LEMOULT (*Compt. rend.*, 1906, 143, 603—605).—The difference between the observed and calculated (Abstr., 1905, ii, 441) heat of combustion of azobenzene is 27 Cal., which represents the thermal characteristic of the azo-complex, $-N:N-$, and if this quantity is added to the calculated heats of combustion of "azo"-compounds containing hydroxyl- or amino-groups, for example, *p*-azoanisole, benzeneazo- β -naphthol, 2:4-diaminoazobenzene, &c., the values thus obtained agree so closely with the observed values as to justify the conclusion that the compounds possess an "azo" ($NR:N\cdot C_6H_4\cdot NH_2$ or $\cdot OH$), and not a "quinonoid" ($NHR\cdot N:C_6H_4:NH$ or O) structure.

M. A. W.

Weighing-bottle for Liquids. K. BUSCHMANN (*Chem. Zeit.*, 1906, 30, 1060).—The bottle, which has a narrow, V-shaped tube for delivering the liquid fused into the side near the bottom, is fitted with a hollow glass stopper, to which is attached an india-rubber sphere. By pressing the rubber sphere any desired quantity of the liquid in the bottle can be delivered through the side tube. By a turn of the stopper, connexion through a groove cut in the neck of the bottle between the sphere and the bottle can be made or cut off at will.

P. H.

Viscosity of Binary Liquid Mixtures. FREDERICK H. GETMAN (*J. Chim. phys.*, 1906, 4, 386—404. Compare Dunstan, *Trans.*, 1904, 85, 817).—The viscosity of a series of mixtures of methyl alcohol and water, benzene and toluene, ethyl ether and benzene, ethyl ether and toluene, ethyl alcohol and benzene, has been measured at several different temperatures. The curves representing the variation of the viscosity with the composition of the mixture exhibit a maximum deviation from the simple mixture rule in the case of methyl alcohol and water. The deviation is considerable for ethyl alcohol-benzene mixtures and comparatively small for the other three mixtures examined.

From the existence of a maximum on the curve for methyl alcohol and water mixtures, it is concluded that the association of a liquid is not diminished when mixed with a second associated liquid. The deviations from the mixture rule in the case of non-associated liquid mixtures indicate that molecular complexity is not the sole determining factor in respect of the viscosity of such mixtures.

With rise of temperature, there is a gradual approximation to the simple mixture rule in the case of all the systems examined.

H. M. D.

Flow of Liquids Through Capillary Spaces. JAMES M. BELL and FRANK K. CAMERON (*J. Physical Chem.*, 1906, 10, 658—672).—The movement of water, alcohol, and benzene through capillary tubes is adequately represented by an equation derived from Poiseuille's formula (*Ann. Chim. Phys.*, 1843, [iii], 7, 50).

The movement of water and potassium chloride solution through strips of blotting-paper and columns of dry soil is found to be in harmony with the formula $y^n = kt$, where y is the distance through which the liquid has moved in time t , and n and k are constants for a given temperature and a given liquid.

Experiments were made on the rate at which dye solutions rise in strips of blotting-paper. The rate at which water travels in blotting-paper is diminished by the presence of sodium eosin, the extent of this effect increasing with the concentration of the latter. The rate at which the paper becomes wet is greater than the rate at which it becomes red, so that a partial separation of solvent and solute is effected (compare Trey, *Abstr.*, 1899, ii, 182). When potassium chloride is present in the dye solution, the rate at which the dye travels through blotting-paper is markedly diminished. Experiments were made also on the rate at which certain dye solutions rise in columns of dry soil. The general results are similar to those obtained for the rise of such solutions in blotting-paper. J. C. P.

Extension of the Theoretical Applicability of Guldberg and Waage's Mass Law. T. BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1906, 10, 521—523).—The mass law is deduced from the gas laws by means of the expression $RT \log P/P_0$, which represents the work done in an isothermal change, and this is obtained from the gas equation $PV = RT$. The author points out that the same expression would be obtained from the equation $P(V-d) = RT$, which holds more generally than the simpler equation, and that therefore the mass law is applicable theoretically to systems for which this equation is valid.

L. M. J.

New Method of Representing Graphically Aqueous Solutions of Two and Three Salts with the same Ion, Reciprocal Pairs of Salts, and Van't Hoff's Investigations on Oceanic Salt Deposits. ERNST JÄNECKE (*Zeit. anorg. Chem.*, 1906, 51, 132—157).—For the graphical method of treating these problems, the numerous diagrams in the original must be consulted. G. S.

Electroaffinity of Anions. II. The Nitrite Ion and its Equilibrium with Nitrate and Nitric Oxide. RICHARD ABEGG and HANS PICK (*Zeit. anorg. Chem.*, 1906, 51, 1—28. Compare Schäfer, *Abstr.*, 1905, ii, 499).—Saturated aqueous solutions of silver nitrite at 0°, 14°, and 25° contain 0.113, 0.189, and 0.260 mol. of salt per litre respectively. The results of an investigation of the solubility product $\text{Ag}^+ \times \text{NO}_2^-$ have been given in a previous paper (*Abstr.*, 1905, ii, 586).

When heated in a closed vessel above 40°, solutions of silver nitrite were decomposed according to the equation $2\text{AgNO}_2 \rightleftharpoons \text{Ag} + \text{NO} + \text{AgNO}_3$.

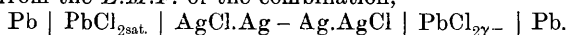
or, on the ionic theory, $\text{Ag}^* + 2\text{NO}_2' \rightleftharpoons \text{Ag} + \text{NO} + \text{NO}_3'$; the action is a reversible one. The constant $k = \frac{P_{\text{NO}}[\text{NO}_3']}{[\text{Ag}^*][\text{NO}_2']^2}$ has the value 1.9×10^5 at 55° , the pressure of nitric oxide being expressed in atmospheres and the concentrations of the other substances in mols. per litre. From this it is calculated that the intensity of the oxidation reaction $2\text{NO}_2' \rightarrow \text{NO} + \text{NO}_3'$ is -0.43 volt, the potential of the hydrogen electrode being taken as zero, in other words, when the substances taking part in the equilibrium are present in unit concentration, the nitrite ion is, by 0.43 volt, a less powerful reducing agent than hydrogen, but the reducing action of the former is greatly increased when the nitric oxide concentration is small. These facts are of great importance in the decomposition relations of nitrites.

The solubility of silver nitrite is increased by the addition of potassium nitrite, and potential measurement show that such solutions contain complex $\text{Ag}(\text{NO}_2)_2'$ ions. The stability constant $k = \frac{\text{Ag}(\text{NO}_2)_2'}{[\text{Ag}^*][\text{NO}_2']^2}$ is 0.68×10^3 .

On the addition of an alkali nitrite to a solution of mercurous nitrite, mercury is precipitated and a mercuric salt remains in solution, the reaction proceeding quantitatively according to the ionic equation $\text{Hg}_2^{++} = \text{Hg} + \text{Hg}^{++}$. It is shown that the mercuric salt is present in solution mainly as a complex ion, $\text{Hg}(\text{NO}_2)_4''$; the constant $k = \frac{\text{Hg}(\text{NO}_2)_4''}{[\text{Hg}^{++}][\text{NO}_2']^4}$ has the value 3.5×10^{13} . This constant is less, and therefore the nitrite complex is less stable than the corresponding halogen compounds of mercury (compare Sherrill, *Abstr.*, 1903, ii, 534, 649). Since, in general, the tendency to complex formation decreases with increasing electroaffinity, it is considered that the nitrite ion is "stronger" than the chlorine ion and this view is also in accord with the considerable solubility of silver nitrite as compared with the halogen silver salts. G. S.

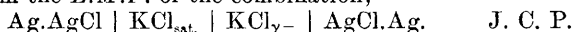
Researches on Chemical Affinity. II. J. N. BRÖNSTED (*Zeit. physikal. Chem.*, 1906, **56**, 645—685. Compare this vol., ii, 339).—The relations between A , the affinity, and U , the heat effect, of a chemical reaction are further discussed, and for the case where the heat effect is a linear function of the temperature, the following formula is deduced: $A = U + (c_2 - c_1)T \log_e T + kT$, in which c_1 and c_2 are the heat capacities of the first and second systems, and k is a constant. Again, if the affinity and heat effect are known for one temperature T_1 , then the value of A at the temperature T is given by the formula. $A = A_1 \cdot T/T_1 - U_1(T - T_1)/T_1 + (c_2 - c_1)[T \log_e T/T_1 - (T - T_1)]$. From this formula it is possible to outline the general character of affinity—temperature curves.

To verify his theoretical deductions, the author has made experiments on the solution affinity of lead chloride and potassium chloride. In the former case, the affinity of the process $\text{PbCl}_{2\text{cryst.}} \rightarrow \text{PbCl}_{2\gamma-}$ (where $\text{PbCl}_{2\gamma-}$ means a solution of the chloride of concentration γ), has been deduced from the *E.M.F.* of the combination,



These measurements confirm the author's formulæ, and it has in especial been found possible to determine the position of a maximum point on the affinity-temperature curve. The experiments with potassium

chloride also supply confirmation of the author's theoretical work. In this case the affinity of the solution process at various temperatures was deduced from the *E.M.F.* of the combination,



Relation of Chemical Activity to Electrolytic Conductivity.

JOHN L. SAMMIS (*J. Physical Chem.*, 1906, 10, 593—625).—When the rate of inversion of a solution containing sucrose, acid, and water is compared with the rate of inversion of a solution containing the same quantities of sucrose and acid, but benzene or acetone instead of part of the water, it is found that the change of velocity and the change of conductivity are quite out of proportion to each other, and not even always in the same direction. Similar experiments on the rate of catalysis of methyl acetate by acids, and on the rate of solution of magnesium in acids, lead to a similar conclusion; that is, the activity of acids in the three foregoing types of chemical action, varies independently of the electrolytic conductivity of the solutions. The acids used were nitric, hydrochloric, and acetic, sometimes in very concentrated, sometimes in dilute solution.

Numerous experiments are described showing that the precipitation of one metal by another from a salt may take place in non-conducting solutions (compare Kahlenberg, *Abstr.*, 1902, ii, 301). Thus, when a solution of copper oleate in amyl nitrate is heated with metallic lead for two hours on the water-bath, the lead is coated with metallic copper. Of 83 solvents examined, 69 are found to permit this precipitation of copper from copper oleate, the solutions being in all cases non-conducting. In the elimination of copper from copper oleate, lead is the most efficient metal. Many metals are without action; thus, sodium can be melted in the toluene solution of copper oleate without producing any effect. Lead is much more reactive with copper oleate than with other metallic oleates, and eliminates copper from other salts such as the hexoate and palmitate. Lead eliminates copper also from the fused salts.

In order that copper may be precipitated by lead from a copper oleate solution, the latter must contain more than a certain percentage of the oleate. This minimum percentage of copper oleate differs for different solvents and for different temperatures. Again, the precipitation of copper from copper oleate solutions by lead is greatly facilitated by the presence of lead oleate, cadmium oleate, or cotton-seed oil.

The experiments recorded are considered to show conclusively that no constant relation exists between electrolytic conductivity and chemical activity. It is maintained that the observed facts are most adequately interpreted when solutions are regarded as chemical unions of solvent and solute.

J. C. P.

Researches on Catalytic Racemisation. CHR. WINTHER (*Zeit. physikal. Chem.*, 1906, 56, 719—749. Compare this vol., ii, 736).—In the racemisation of *d*-tartaric acid the first product is exclusively *i*-tartaric acid, and racemic acid is not formed directly. Measurements of rotation recorded in the paper make it probable that the catalytic

effect of alkalis in accelerating racemisation is associated with the replacement of hydroxylic hydrogen by metals. A compound of this kind, disodium sodiotartrate, $\text{CO}_2\text{Na}\cdot\text{CH}(\text{ONa})\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{Na}$, has been isolated from the strongly alkaline solutions of sodium tartrate, and found to have a transition point at 51.5° .

Potassium does not so readily form such a compound, and in harmony with this it is found that potassium hydroxide does not have as marked a catalytic effect on racemisation as sodium hydroxide.

Incidentally, a method is described for the investigation of strongly alkaline solutions, depending on the determination of the rate at which phenolphthalein solutions are decolorised (compare McCoy, *Abstr.*, 1904, ii, 512). This method was devised in the course of an attempt to establish a relationship between the rate of racemisation and the number of hydroxyl ions present. Although the attempt was unsuccessful, it was found that the number of hydroxyl ions in strong potash or soda solutions is generally increased by the addition of potassium or sodium salts, the increase effected by potassium salts being greater than the increase effected by sodium salts. J. C. P.

Retarding or Paralysing Action Exerted by Chloroform, &c., on the Reactions yielding Organo-magnesium Compounds. ALBERT REYCHLER (*Bull. Soc. chim.*, 1906, [iii], 35, 803—811).—When chloroform is added (1) before the alkyl haloid in the Grignard reaction, or (2) to a mixture in which a reaction of this type is already proceeding, or (3) to a mixture in which such a reaction has been started by the addition of a small quantity of an exciting agent to the liquid consisting of ether, alkyl haloid, and magnesium, the reaction is inhibited either temporarily or permanently, depending on the quantity of chloroform used. A similar retardation or paralysis is brought about by the addition of carbon tetrachloride, bromoform, acetone, or ethyl acetate, although the last of these appears to exercise an accelerating action in the case of a mixture of magnesium, methyl iodide, and ether.

If the Grignard reaction may be regarded as a fermentative process, starting at a particular point and being propagated through the mass by reaction between contiguous molecules, the retarding action of chloroform may be explained by (1) the dilution of the liquid and (2) the interposition of foreign particles between molecules which would otherwise react. Experiments designed to test the validity of this view gave negative results.

It is suggested therefore that the production of organo-magnesium compounds is accompanied by the formation of catalytic substances capable of initiating changes of the type by which they themselves are produced, and of rendering active systems which would otherwise remain inert. These catalytic agents, possibly substances of the type MgR_2 , are probably highly reactive towards chloroform and the addition of the latter therefore leads to a retardation of the whole reaction.

T. A. H.

Substances existing in Three Liquid Modifications, One Isotropic and Two Fluid-Crystalline. OTTO LEHMANN (*Zeit. physikal. Chem.*, 1906, 56, 750—766).—Cholesteryl decoate is found

not only to behave as a crystalline fluid between 82.2° and 90.6° , but to exist in two modifications within these limits of temperature. The change from the one modification to the other has been observed under the microscope, as the substance separated from solution in a mixture of aniline and amyl alcohol. That this is a case of true dimorphism is further shown by studying the effect of foreign admixtures, but for the detailed evidence of the transition, the original must be consulted.

Two fluid crystalline modifications appear to exist also in the following cases: cholesteryl octoate, isovalerate, isobutyrate, *n*-valerate, propionate, hexoate, butyrate, and formate. J. C. P.

Extension of the Field of Existence of Fluid Crystals by Addition of other Substances. OTTO LEHMANN (*Ann. Physik*, 1906, [iv], 21, 181—192. Compare preceding abstract).—Supercooled ammonium oleate exhibits the properties of fluid crystals, but has a very fleeting existence and is very readily converted into the stable solid form. The stability, however, of the fluid crystalline ammonium oleate is increased by adding the isomorphous potassium and sodium oleates or trimethylamine oleate. In the case of cholesteryl acetate the fluid crystalline monotropic modification can be obtained only from the supercooled liquid, but by addition of cholesteryl benzoate the field of existence of the enantiotropic modification is enlarged. Other substances, which do not normally yield fluid crystals, but can be obtained in that form by a small addition of another substance, are *p*-azophenetole and *p*-azoanisole. Further, benzyl *p*-azoxycinnamate (Vorländer, this vol., ii, 318) can be made to appear as fluid crystals by addition of ethyl *p*-azoxybenzoate. J. C. P.

Spiral Arrangement in Crystallised Substances. FRÉDÉRIC WALLERANT (*Compt. rend.*, 1906, 143, 555—557).—Michel Lévy has shown that in some spherulites of chalcedony the optical orientation of the fibres varies continuously along their length; this may be explained by assuming the fibres to have a helical twist about their long axis. A similar phenomenon was observed by the author in several artificially crystallised substances, especially when two substances have been hurriedly crystallised together in the form of spherulites. Sodium nitrate and sodium bromate, which although isomorphous only yield mixed crystals within certain limits, produce such spherulites when fused together. With malonamide and *p*-azoxyanisole the helical twist appears to be determined by the presence of antonic acid, and in the case of chalcedony the water may have had a similar influence. L. J. S.

Liquid Crystals of Cholesteryl Propionate. FRÉDÉRIC WALLERANT (*Compt. rend.*, 1906, 143, 605—606).—Cholesteryl propionate exists in two solid modifications, one unstable and slightly doubly refracting, and the other biaxial and highly doubly refracting. The latter frequently crystallises in spherulites, the fibres forming a spiral round one of the bisectors of the optic axes; if such a crystal is carefully heated, it is converted into a uniaxial liquid crystal which exhibits

the same spiral formation and has its optic axis parallel to the mean axis of the solid crystal.

The author finds that the property of diffusing a coloured light, observed by Reinitzer in the case of liquid crystals, is confined to sections which are perpendicular to the optic axis, and if the crystal is fused and allowed to cool gradually it is somewhat suddenly converted into liquid crystals in the form of a radiating star which exhibit the phenomenon of the black cross and do not diffuse light, the fibres being parallel to the optic axis; on removing the cover glass the stellate clusters are destroyed, and the liquid becomes homogeneous and diffuses light from all points of its surface. M. A. W.

Liquid Crystals of Ammonium Oleate. FRÉDÉRIC WALLERANT (*Compt. rend.*, 1906, 143, 694—695).—Liquid crystals of ammonium oleate exhibit in convergent polarised light a good uniaxial interference figure, the optical sign of which is positive. The alterations of the optical character with changes of temperature indicate that there are four crystalline modifications of this compound. L. J. S.

Connexion between the Critical Temperatures of Gases and Vapours and their Absorption Coefficients, and the Viscosity of the Solvent Medium. WM. TATE (*Medd. k. Vetensk. Akad. Nobelinstitut*, 1906, 1, No. 4, 1—9. Compare Winkler, *Abstr.*, 1892, 556; this vol., ii, 342; Rex, this vol., ii, 342).—The relationship enunciated by Winkler that the change in the absorption coefficient of a gas with the temperature is proportional to the change in the viscosity of the solvent is shown to be at variance with experimental data. The value of the constant in Winkler's equation (*loc. cit.*) is not determined by the number of atoms in the molecule of the gas.

It is shown that the data of Winkler and Rex satisfy, however, the relationship, $K = (\mu_0 - \mu_t/\mu_0) \cdot (\beta_0/\beta_t - \beta_t) \cdot (\sqrt{T_k/T_w})$, in which μ_0 and μ_t denote the coefficients of viscosity of water, β_0 and β_t the absorption coefficients of the gas at 0° and t° respectively, T_k the critical temperature of the gas and T_w the mean temperature of the solution. For gases with very different critical temperatures the value of K is very approximately 0.90 for the temperature interval 0—20°. The relationship may inversely be employed to deduce the critical temperature of a gas or vapour from the variation of its absorption coefficient with the temperature. H. M. D.

Apparatus for Measuring the Solubility of Solids in Liquids. P. P. VEIMARN (*J. Russ. Phys. Chem. Soc.*, 1906, 38, i, 228—234).—The apparatus here described depends on the same principle as that of Victor Meyer, but differs from all others so far devised in the following features. (1) The total absence of glass taps or rubber joints in contact with the liquid under investigation. (2) The rapidity with which small quantities can be removed for trial. (3) No suction need be applied, whatever the nature of the substances employed. (4) The filtration can be observed and regulated easily. (5) Filtration need not be resorted to when the solid settles easily to the bottom of the vessel. A figure and a full description of the apparatus and the method of working it are given. Z. K.

The Mechanism of Ionisation by Solution. GUSTAV HINRICHS (*Compt. rend.*, 1906, 143, 549—550).—A theoretical paper in which the following explanation is advanced of the phenomena of solution and ionisation. When sodium chloride dissolves in water its molecules are separated from one another by the mechanical action of the rapidly rotating molecules of the water. The friction thus set up produces statical electricity which cannot escape owing to the water being a non-conductor, the two atoms of the salt molecule become charged, the sodium atom receiving the positive and the chlorine atom the negative electron, dissociation of the chemical combination of the two atoms then occurs, and the atoms, each charged with an electron, become the ions.

M. A. W.

Solution of Metals. III. TYCHO ERICSON-AURÉN and WILHELM PALMAER (*Zeit. physikal. Chem.*, 1906, 56, 689—702. Compare Abstr., 1902, ii, 64; 1903, ii, 718).—A reply to Brunner (Abstr., 1905, ii, 235), and a criticism of the latter's diffusion theory of solution as applied to metals.

J. C. P.

The Separation of Liquids into Layers. F. W. SMIRNOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, i, 5—6).—At a given temperature the effect of any one group of metals on the separation of isobutyric acid and water into layers increases with decreasing atomic weight of the metal; the effect also increases on passing from the first to the second group, and from the second to the third. For acid radicles the effect increases in the order: NO_3 , Br, $\text{SO}_4/2$, Cl; KI decomposes. The action of a salt is due to its tendency in solution to become associated with the solvent. Thus the greater the tendency of the radicles or elements to form such associations, the less will be the amount required to induce separation.

Z. K.

Agglutination and Allied Reactions from the Physical Standpoint. I. B. H. BUXTON and PHILIP SHAFFER (*Zeit. physikal. Chem.*, 1906, 57, 47—63).—For a number of electrolytes the smallest concentrations which suffice to cause the coagulation of mastic, bacteria, and agglutinin bacteria are tabulated, and the results are on the whole in good agreement with those of Bechhold (Abstr., 1904, ii, 650). The factors generally considered to govern the efficiency of the positive ion in causing flocculation are (1) the degree of electrolytic dissociation, (2) the valency, (3) the mobility of the ion, (4) the electrolytic solution tension. To these the authors add hydrolysis as an important factor.

Coagulation is not due alone to mere neutralisation of the charges carried by the colloid, and probably the ability of the colloid particles to adsorb electrolytes or to form solid solutions comes into play. The authors' experiments indicate that in some cases, such as the coagulation of mastic by lead salts, there is a permanent union between the electrolyte and the suspension.

Bacteria and agglutinin bacteria when suspended in water are alike in that they both travel to the anode under the influence of an electric

current, but the suspension of the latter is much less stable than that of the former.

In studying the action of those electrolytes which cause the coagulation of bacteria, the authors find that the flocculation takes place only when the concentration of the electrolyte lies between certain limits. Solutions of the electrolyte outside this zone, either more concentrated or more dilute, fail to cause precipitation. On the other hand, the behaviour of iron, chromium, and aluminium salts in regard to the coagulation of mastic is peculiar, in that there are certain gaps in the concentration of the electrolyte within which no flocculation takes place.

J. C. P.

Agglutination from the Physical Standpoint. II. A Comparison of various Suspensions. B. H. BUXTON and OSCAR TEAGUE (*Zeit. physikal. Chem.*, 1906, 57, 64—75).—The work described in the previous abstract has been extended by the study of other suspensions. The general conclusions are in harmony with the results already recorded.

J. C. P.

Agglutination from the Physical Standpoint. III. The Electrical Charge carried by the Suspended Particles. OSCAR TEAGUE and B. H. BUXTON (*Zeit. physikal. Chem.*, 1906, 57, 76—89. Compare the two preceding abstracts).—Unorganised suspensions, bacteria and agglutinin bacteria, all carry a negative charge and travel towards the anode when in pure water. In presence of an electrolyte, however, and subject to certain conditions of concentration, the charge on the suspensions of bacteria becomes a positive one. The theory of this is discussed in the paper.

J. C. P.

Nature of Coagulation. NICOLA PAPPADÀ (*Gazzetta*, 1906, 36, ii, 259—264).—Since hydrogels precipitated by electrolytes contain only the colloidal matter and not the electrolyte, the change cannot be due to chemical reactions, but must depend solely on catalytic processes. The precipitation is not brought about merely by diffusion, because non-dissociated, dissolved, diffusible organic substances are devoid of this power of coagulation.

The author's investigations of the coagulation of dilute, colloidal solutions of silicic acid, prussian blue, copper ferrocyanide, and silver show that: (1) the coagulating action of electrolytes with univalent cations increases with the velocity of hydro-diffusion of the latter. The following series gives these cations in decreasing order of magnitude of either their velocity of hydro-diffusion or their coagulating action: H, Cs, Rb, K, NH_4 , Na, Li; in the case of silicic acid, hydrogen is an exception. (2) For electrolytes with bivalent cations, the coagulating action varies in the same way, but is greater than with electrolytes having univalent cations. (3) The same is the case with electrolytes containing trivalent cations. It is concluded that the coagulating action of an electrolyte depends only on the velocity of diffusion and the electric charge of the cations.

Bacteria are precipitated in the same manner as inorganic suspensions and colloids, and they are also transported towards the anode by

an electric current, so that they, too, must have a negative electric charge.

The reason for water becoming positively charged and proceeding towards the cathode, whilst the suspended particles pass in the direction of the anode, rests on the experimental observation that substances having a high dielectric constant, when in contact with other substances having a lower dielectric constant, become positively charged.

The mechanism of the precipitation of a colloid by an electrolyte is explained as follows: the electrolyte diffuses in the form of ions into the solution of the colloid, the particles of which are impermeable to the ions, and hence receive blows tending to withdraw from the particles their condition of minute suspension, the time required for this depending on the velocity of diffusion of the ions. Ions charged with positive electricity neutralise the negative charges of the particles, the charges of the same cations being re-established by the water giving up its charge to them. Suspension of the particles being only possible when they carry a negative charge, precipitation must ensue

T. H. P.

Action of Electrolytes on Colloidal Solutions. E. F. BURTON (*Phil. Mag.*, 1906, [vi], 12, 472—478).—Coagulation of colloids takes place most rapidly at the isoelectric point, that is, when the colloid particles are uncharged and do not move in an electric field. The effects of uni-, bi-, and ter-valent ions in this respect differ greatly, the coagulative powers, according to the results of Linder and Picton, being 1 : 35 : 1023 (*Trans.*, 1895, 67, 63), these values being also in accord with Whetham's theoretical deduction. The coagulative power of quadrivalent ions, however, was found by Linder and Picton to be small, a result not in accord with the theory (*Trans.*, 1905, 87, 1906). The author's experiments with colloidal solutions of silver and gold prove that the addition of aluminium sulphate in small quantities causes first a decrease in the charge of the particles and ultimately a reversal. The solution passes, at the isoelectric point, through a state of maximum instability, becoming again stable when more of the electrolyte is added, and the author suggests that it is possible that with the quadrivalent ions the isoelectric point is so easily overstepped that its existence might be easily overlooked and the coagulative power hence greatly underestimated. The charge on the colloidal silver is calculated as equal to 0.04 of that on the equivalent amount of a univalent ion, the corresponding number in the case of colloidal gold being 0.12.

L. M. J.

Literature of the Colloids. ALEXANDER P. SABANÉEFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, i, 141—144).—A criticism of the bibliography of the colloids by Müller (*Abstr.*, 1904, ii, 392).

Z. K.

Vacuum Distilling Apparatus for Solid Substances. HUGO HAEHN (*Zeit. angew. Chem.*, 1906, 19, 1669—1670).—The Brühl apparatus is recommended, but the exit tube of the Claisen fractionating flask is connected with a condenser which projects into the

receiver chamber. Through the condenser hot paraffin oil is circulated, so that the inner tube of the condenser can be kept at a temperature higher than the melting point of the substance distilling. A figure of the apparatus is given in the original. L. DE K.

Safety Condenser for Extractions with Inflammable Solvents. ADOLPHE BESSON (*Chem. Centr.*, 1906, ii, 993; from *Collegium*, 1906, 222—223).—The upper end of the reflux condenser is fitted with a cork, through which passes a tube, bent so that it may be connected by a rubber tube to an opening in the water jacket of the condenser. If, owing to too vigorous boiling, the solvent should rise to the top of the condenser, it passes into the jacket and is carried away by the water. An additional opening in the water jacket serves to hold a water trap. P. H.

Simple Modification of a Soxhlet Condenser for Recovering the Solvent. NAPOLEONE PASSERINI (*Chem. Centr.*, 1906, ii, 993; from *Staz. sperim. agrar. ital.*, 39, 33—34).—The lower end of the reflux condenser, which is connected to a Soxhlet extraction apparatus by means of an adapter, is bent so as to admit of its being turned through an angle of 180° , and used as an ordinary condenser for distilling off the solvent. P. H.

Inorganic Chemistry.

Autoxidation and Oxidation with Nitric Oxide. WILHELM MANCHOT (*Ber.*, 1906, **39**, 3510—3511).—When organic dihydro-compounds such as oxanthranol, indigo-white, and hydrazobenzene undergo autoxidation, the reaction occurs according to the following equation: $\text{RH}_2 + \text{O}_2 = \text{R} + \text{H}_2\text{O}_2$, a molecule of hydrogen peroxide being formed for each molecule of oxygen absorbed. That this formation of hydrogen peroxide is due to the two linked oxygen atoms, and that this chain is still intact in the peroxide itself may be shown by the fact that when the oxidation is effected by a substance not containing linked oxygen, then the formation of peroxide does not occur. A convenient oxidising agent for this demonstration is nitric oxide, which reacts in accordance with the following equation: $\text{RH}_2 + 2\text{NO} = \text{R} + \text{H}_2\text{O} + \text{N}_2\text{O}$.
G. T. M.

Electrolytic Chlorine. PAUL FERCHLAND (*Chem. Centr.*, 1906, ii, 1157—1158; from *Elektrochem. Zeit.*, 1906, **13**, 114—119).—In spite of frequent statements to the contrary, electrolytic chlorine is identical with chlorine prepared by other processes. The peculiar action of this chlorine in the preparation of bleaching powder is attributed to its containing carbon dioxide derived from the oxidation of the electrodes.

Chlorine prepared by the electrolytic process contains from 10 to 12 per cent. of carbon dioxide; this seems to be due, not to secondary reactions, but to a wandering of the ions—some of the hydroxyls from the alkali passing through the diaphragm to the anode; if two diaphragms are used, the space between them becomes alkaline. The amount of carbon dioxide in the cathode space is in practice never less than 6 per cent., even when the potassium chloride is still fresh, but it can be reduced to 1 or 2 per cent. by employing two diaphragms and maintaining a continuous circulation of potassium chloride. At lower temperatures, which are not attainable on a large scale, more oxygen than carbon dioxide is obtained and also a little carbon monoxide; at higher temperatures, the electrodes are attacked by the oxygen.

P. H.

Equilibrium in the Deacon Process. GILBERT N. LEWIS (*J. Amer. Chem. Soc.*, 1906, 28, 1380—1395).—A method has been devised for determining the condition of equilibrium of the reaction $4\text{HCl} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{Cl}_2$ at different temperatures. The apparatus is described with the aid of a diagram.

The catalyst, cupric chloride, does not reach a constant state for several days, and it is therefore necessary to pass a mixture of given composition over it until a stationary condition is attained. The time required to establish equilibrium in the gases was found to increase as the temperature was diminished and as the proportion of oxygen was reduced. Experiments were made at 352° , 386° , and 419° with mixtures of oxygen and hydrogen chloride in various proportions. The results obtained at a constant temperature were found to be in accordance with the law of mass-action. The yield of chlorine from a given mixture is greater the lower the temperature, and the change of the equilibrium constant is in good agreement with van't Hoff's equation $d\ln K/dT = Q/RT^2$, where K is the equilibrium constant in terms of partial pressures, T the absolute temperature, R the gas constant, and Q the total heat developed when the reaction occurs at constant pressure. It is shown that the equilibrium constant of the Deacon reaction at any temperature can be calculated from the equation $\log K = (1509/T) - 1.811$. The value thus obtained at 1537° agrees with Löwenstein's results (this vol., ii, 272) on the dissociation of water and hydrogen chloride at that temperature.

From the equilibrium constant of the Deacon reaction at 25° and the free energy of formation of hydrogen chloride as calculated from Dolezalek's results (*Abstr.*, 1898, ii, 421), the *E.M.F.* of the hydrogen-oxygen cell is found to be 1.207 volts, a value which is in good agreement with that obtained by an entirely different method described in an earlier paper (this vol., ii, 262).

E. G.

The Existence of Bromine Chloride. PAUL LEBEAU (*Compt. rend.*, 1906, 143, 589—591).—When a mixture of bromine and chlorine in equivalent quantities is cooled at -58° it separates into a liquid and a solid phase containing 32 and 24.84 per cent. of chlorine respectively, the percentage of chlorine in the original mixture being 30.71. Further, if the mixture is cooled to -80° and saturated with

chlorine, an orange-red liquid is obtained which deposits mixed crystals of bromine and chlorine when heated at different temperatures and then cooled. Finally, the cooling curve of mixtures of chlorine and bromine consists of a slightly concave line joining the melting points of bromine (-7.3°) and chlorine (-102.5°), but showing no maximum points; it follows, therefore, that bromine and chlorine form mixed crystals, but that no compound of the two elements exists. The so-called "bromine chloride" of Bornemann (Abstr., 1878, 11) and the "bromine trichloride" of Thomas and Dupuis (this vol., ii, 662) are respectively a solution of chlorine in bromine and mixed crystals of the two elements.

M. A. W.

The Liquefaction of Air by Expansion with Performance of External Work. GEORGES CLAUDE (*Compt. rend.*, 1906, 143, 583—584).—When the liquefying apparatus previously described (this vol., ii, 16, 17) is fed with cooled oxygen below its critical pressure instead of with cooled and compressed air, the efficiency of the machine is increased in the ratio of 0.95:0.85, and the oxygen thus employed is recovered at a later stage of the operation and can be used again for the same purpose.

M. A. W.

Mixtures of Liquid Oxygen and Nitrogen. ALFRED STOCK and CARL NIELSEN (*Ber.*, 1906, 39, 3393—3397. Compare Erdmann and Bedford, Abstr., 1904, ii, 557; Inglis and Coates, Trans., 1906, 89, 886).—When a mixture of pure liquid oxygen and nitrogen is allowed to boil for some time a residue of pure oxygen is obtained. The oxygen was prepared from a mixture of potassium chlorate and manganic oxide and the nitrogen from a solution of sodium nitrite, ammonium chloride, and potassium dichromate. The gases were liquefied by means of liquid air through which a rapid stream of hydrogen was bubbled. Thirty c.c. of a mixture containing 11.6 per cent. of nitrogen when evaporated to 7 c.c. contained no nitrogen. When liquid nitrogen and oxygen in molecular proportions are mixed at -197° an increase in temperature of 0.5° and a decrease in volume of about 0.5 per cent. can be observed.

J. J. S.

Preparation of Ozone. CARL D. HARRIES (*Ber.*, 1906, 39, 3667—3670. Compare this vol., i, 225, and Jannasch, this vol., ii, 577).—In the preparation of ozone, ten Berthelot tubes have been used (*a*) in parallel and (*b*) end to end. When the oxygen passes through at the rate of 0.5 litre per minute, the yield of ozone is much the same in the two cases, namely, some 10 per cent. When only five tubes are used, the second arrangement gives somewhat the better yield and the same holds good when the rate of flow is increased to 1 litre per minute, but in both sets of experiments the results are low compared with the yields obtained with ten tubes and the slower rate of flow. With a flow of 0.2—0.25 litre per minute and ten tubes end to end, the percentage of ozone can be raised to thirteen. The system of parallel tubes is more convenient although the yields of ozone are smaller.

J. J. S.

Thermal Relationships between Ozone, Nitric Oxide, and Hydrogen Peroxide. I. FRANZ FISCHER and HANS MARX (*Ber.*, 1906, 39, 3631—3647. Compare Fischer and Braehmar, this vol., ii, 224; Fischer and Mark, *ibid.*, ii, 606; Warburg and Leithäuser, *ibid.*, ii, 740).—Dried and purified air was admitted through a slit 10 mm. long and 1 mm. wide to a Nernst filament (0.5 ampere) placed 1 mm. from the slit. The tube containing the filament was surrounded with cold water and the issuing gases tested by means of tetramethyl-*p*-diaminodiphenylmethane (this vol., ii, 627). The colour changes show that when the rate of flow of the air is small, 2.8 m. per second, nitric oxide is the chief product formed, but with a rate of 6.2 m. per second, mainly ozone is formed. The change occurs when the rate is about 5.2 m. per second. The time required to give the coloration diminishes rapidly as the rate of flow increases. With moist air, the formation of ozone can only be observed with a higher velocity, namely, 7.3 m. per second, and even then only very slowly. With a velocity of 31 m. per second no trace of nitric oxide is produced. When moist air is used, hydrogen peroxide is formed in addition to, and also in place of, ozone. This peroxide condenses with the water in the cold tube and does not pass out with the ozone. The following values have been obtained for air containing varying amounts of water vapour:

	O ₃ titre.	H ₂ O ₂ titre.
Dried with phosphoric anhydride.....	1.12	—
„ „ concentrated sulphuric acid	0.90	—
„ „ 48 per cent. „ „	0.105	—
Passed through water at 11.3°	0.070	0.011
„ „ „ „ 36°	0.054	0.031
„ „ „ „ 60°	0.039	0.074

These numbers indicate that the first traces of moisture lessen the yield of ozone by catalytic action, whereas larger quantities of water vapour gradually increase the yield of hydrogen peroxide at the expense of the ozone.

The influence of the rate of flow of dry air on the yield of ozone has been investigated. The best yield was obtained with a velocity of 57—63 mm. per second, namely, 0.02 per cent. of the air used. The paper concludes with a statement of the best conditions under which ozone, hydrogen peroxide, or nitric oxide alone or a mixture of any two or of all three may be most readily obtained by heating and subsequent cooling of air, with or without moisture. J. J. S.

Molecular Weights of certain Inorganic Substances. ERNST BECKMANN (*Zeit. anorg. Chem.*, 1906, 51, 96—115. Compare Abstr., 1904, ii, 235).—The molecular weight of aluminium bromide in bromine corresponds with the formula Al₂Br₆ both at the boiling and freezing points. Sulphur enters into chemical combination with bromine, giving S₂Br₂ molecules, whilst sulphuryl chloride, S₂Cl₂, has the normal molecular weight in the same solvent.

The boiling-point elevation constant for chlorine, determined by using perchloroethane, C₂Cl₆, and carbon tetrachloride as solutes, is 16.5.

When freshly dissolved in liquid chlorine, sulphur is present as S_8 molecules, but it slowly changes into sulphuryl chloride. The latter has the normal formula S_2Cl_2 in boiling chlorine, but at higher temperatures undergoes partial decomposition with formation of reddish-brown sulphur dichloride, SCl_2 , which also has the normal formula in this solvent.

Sulphur and selenium seem to form monoatomic molecules in dilute solution in sulphuryl chloride. The elevation constant for the latter solvent is about 5° .

The molecular weights of stannic iodide and antimony and arsenic tri-iodides in tin tetrachloride, and in phosphorus, arsenic and antimony trichlorides, are abnormally small (one-third to one-half the normal values), as is the molecular weight of arsenious oxide, As_4O_6 , in the two last-mentioned solvents. Other observers (Walden, *Abstr.*, 1902, ii, 247; Garelli and Bassani, *Abstr.*, 1901, ii, 541) have obtained corresponding results by the cryoscopic method, and it is suggested that the anomalies are largely due to chemical combination between solvent and solute and, to some extent, to ionisation.

In tin tetrachloride and arsenic trichloride, sulphur gave results pointing to the formula S_8 . G. S.

Surface Tension of Fused Sulphur. H. ZICKENDRAHT (*Ann. Physik.*, 1906, [iv], 21, 141—154).—One end of a glass tube of known diameter was kept under the surface of the fused sulphur, and the pressure which just sufficed to force bubbles of some gas from the end of the tube was determined. From the radius of the tube and the observed pressure, the surface tension was calculated. From the melting point up to 160° there is a gradual fall in the value of the surface tension. At 160° a minimum value of about 6 mg. per mm. is reached, and thereafter there is a rise up to a maximum about 250° , at which temperature the value of the surface tension is about 12 mg. per mm. After the maximum there is a rapid fall in the surface tension to about 300° , and subsequently a gradual fall may be observed up to the boiling point of the sulphur, at which temperature the surface tension is about 4.5 mg. per mm. In view of the results obtained the author suggests that above 160° a new modification of sulphur exists—a modification to which the name of δ -sulphur is given. J. C. P.

Sulphuric Acid Contact Process. LOTHAR WÖHLER, A. FOSS, and W. PLÜDDEMANN (*Ber.*, 1906, 39, 3538—3549).—When a mixture of sulphur dioxide and oxygen is passed under comparable conditions over asbestos charged with (1) platinum, (2) platinum monoxide, or (3) platinum dioxide, the catalytic efficiency of the metal is found to exceed that of either oxide. The activity of the asbestos charged with the oxides increases as time goes on, and this increased efficiency is the consequence of gradual reduction of the oxides. A comparison of palladium and palladium monoxide gave a similar result. The authors find further that whereas of the three metals, platinum, palladium, and iridium, the first-named forms the least stable oxides, and the last-named the most stable oxides, the temperature of maximum catalytic efficiency is lowest for platinum and highest for palladium. It thus appears that the catalytic action of the platinum metals in the

contact process is not due to the intermediate formation of an exothermic oxide. The observations, however, might be accounted for by the existence of an endothermic oxide formed at high temperatures.

J. C. P.

Vapour Tension of Liquid Ammonia. OTTO BRILL (*Ann. Physik.*, 1906, [iv], 21, 170—180).—The vapour tension of solid ammonia at -79.2° , determined by a dynamical method, is 36.5 mm. of mercury. By a statical method the values of the vapour tension of liquid ammonia have been determined at other temperatures up to -33° . The melting point of ammonia is -77.7° ; the boiling point under atmospheric pressure is -33.0° .

The author uses his results to test a formula deduced recently by Nernst (*Göttinger Nach.*, 1906) for the variation of vapour tension with temperature, and finds a good agreement between the calculated and the observed values of the vapour tension. Ammonia behaves as a slightly associated liquid.

J. C. P.

Red Phosphorus. A. SIEMENS (*Chem. Centr.*, 1906, ii, 1084—1085; from *Arb. Kais. Ges.-A.*, 1906, 24, 264—304).—Mitscherlich's test cannot be regarded as absolutely conclusive for the presence of traces of yellow phosphorus in the red variety, inasmuch as red phosphorus itself is able to produce a similar although very much fainter luminosity. There is no chemical reaction characteristic for yellow phosphorus alone, which is not exhibited in less degree by red phosphorus, but the reaction velocity of red phosphorus is much slower than that of yellow phosphorus. The glowing of phosphorus is attributed to the formation of a volatile low oxide of phosphorus. In order to detect yellow phosphorus in red phosphorus, 5 grams of the substance should be extracted for half an hour with 150 c.c. of benzene. One c.c. of the cooled filtered solution is then mixed with 1 c.c. of a solution of 1.7 grams of silver nitrate in 100 c.c. of ammonia solution of sp. gr. 0.992. Samples of pure red phosphorus give, after the lapse of not more than half an hour, only a faint yellow coloration, whereas a precipitate is formed if any yellow phosphorus was present.

Red phosphorus is not converted into the yellow variety by shock. When red phosphorus is powdered or shaken, it is converted into a more finely divided condition in which it is more soluble and also more reactive than the ordinary red variety. A solution of the more soluble form left in contact with unchanged red phosphorus slowly deposits its phosphorus, whereas a solution of yellow phosphorus remains unchanged under similar conditions. A saturated benzene solution of red phosphorus, evaporated to dryness with dilute nitric acid, leaves a yellowish-red solid, which is very slightly soluble in aqua regia; the solution is not precipitated by ammonium molybdate or magnesia mixture, but is turned yellow by ammonia, owing most probably to the formation of picric acid. Yellow phosphorus treated in the same way yields a solution which gives reactions for phosphoric acid. On evaporating a benzene solution of yellow phosphorus, a tough, yellow, wax-like solid with a very unpleasant odour remains behind, which, when left in contact with red phosphorus and exposed to the light, is slowly

converted into red phosphorus. A benzene solution of red phosphorus evaporated in the same way behaves quite differently. P. H.

Hypophosphoric Acid. NICOLA PARRAVANO and C. MARINO (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 305—311. Compare this vol., ii, 744).—By means of conductivity and transport measurements, the authors show that hypophosphoric acid has the formula $H_4P_2O_6$, and that it is resolved in solution into the three ions, H , H , and $H_2P_2O_6$; further, that normal sodium hypophosphate combines in solution with molybdic and tungstic anhydrides, forming complex molybdo- and tungsto-hypophosphates. T. H. P.

Dissociation of Water-Vapour and Carbon Dioxide at High Temperatures. IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1906, 28, 1357—1379. Compare Nernst and Wartenberg, *Abstr.*, 1905, ii, 629).—Experiments are described which were undertaken with the object of investigating the dissociation of water-vapour and carbon dioxide around glowing platinum wires. The apparatus employed is described with the aid of a diagram. The method is simple and rapid, the only serious difficulty being the determination of the temperature of the wire.

It has been found that the amounts of the dissociation products, obtained when water-vapour or carbon dioxide is passed through a tube containing a glowing platinum wire, corresponds with the dissociation equilibrium at the temperature of the wire. The degree of dissociation found in the case of water-vapour was 9.5 per cent. lower than that obtained by Nernst and Wartenberg (*loc. cit.*) and 7 per cent. lower in the case of carbon dioxide. The temperature-coefficient of the electrical resistance of pure platinum was determined for temperatures up to 1200°. It was found that below 1300° platinum and platinum-rhodium wires do not disintegrate in water-vapour or carbon dioxide, but in water-vapour at 1400° a platinum-rhodium wire begins to disintegrate.

The method is recommended for the determination of dissociation under high pressures. It could also be used for measuring the temperature of platinum wires, since it would only be necessary to surround the wire with water-vapour and then to withdraw some of the water-vapour and analyse it. E. G.

Carbon Diselenide. A. VON BARTAL (*Chem. Zeit.*, 1906, 30, 1044—1045).—An attempt to prepare carbon diselenide by passing carbon tetrachloride vapour over cadmium selenide, heated to a dull red heat, resulted in the formation of a mixture of hexachloroethane, selenium chloride, selenium, and a trace of carbon diselenide; the latter was detected by heating a solution of the substance in carbon tetrachloride with alcoholic potassium hydroxide, and so converting it into potassium selenoxanthate, which was analysed. P. H.

New Determination of the Atomic Weight of Potassium. THEODORE W. RICHARDS and ARTHUR STAEHLER (*Ber.*, 1906, 39, 3611—3625. Compare Richards and Archibald, *Abstr.*, 1903, ii, 366; Richards and Wells, *Abstr.*, 1905, ii, 450).—It having been proved that, starting with a mixture of rubidium, caesium, sodium, and

potassium nitrates, the last salt could be obtained almost pure after two recrystallisations aided by centrifugal draining (Richards, *Abstr.*, 1905, ii, 238), portions of potassium nitrate were purified by five to eleven recrystallisations, at first in Jena glass and afterwards in platinum vessels. The pure potassium nitrate was then converted into the chloride by seven to twelve precipitations by means of hydrogen chloride, from the concentrated aqueous solution at 0° , in a platinum vessel. Under these conditions only small amounts of potassium platinichloride are formed, and are almost completely insoluble in the concentrated potassium chloride solution. The potassium chloride so prepared was proved by spectroscopic examination, to be free from sodium.

The determinations of the ratios $\text{KCl}:\text{AgCl}$ and $\text{KCl}:\text{Ag}$ were made in the same manner as those of the ratios $\text{NaCl}:\text{AgCl}$ and $\text{NaCl}:\text{Ag}$ (Richards and Well, *loc. cit.*). The potassium chloride was fused in a current of dry nitrogen in a porcelain tube and weighed in a platinum bottle fitted with a platinum stopper, as it is too hygroscopic to permit of weighing in an open vessel. The risk of occlusion of silver nitrate in the silver chloride precipitate was diminished by adding at first only the calculated quantity of the silver salt and completing the precipitation by means of a slight excess when the main portion of the precipitate had settled.

The conditions observed in the precipitation and filtration, and the determination of the silver chloride dissolved in the washings are described.

The results of eight experiments with three samples of potassium chloride, prepared by different numbers of precipitations, gave for the ratio $\text{KCl}:\text{AgCl}$, an average of 0.520118:1.

In nine experiments for determining the ratio $\text{KCl}:\text{Ag}$, with five different samples of potassium chloride, the results gave an average of 0.691072:1.

If the atomic weight of silver is taken as 107.93, and that of chlorine as 35.473, the results of both the above series of experiments make the atomic weight of potassium to be 39.114. G. Y.

Electrolysis of Alkali Chlorides with Alternating Currents.

II. ANGELO COPPADORO (*Gazzetta*, 1906, 36, ii, 321—328. Compare this vol., ii, 214).—The formation of chlorate by the electrolysis, with a current of forty-two alternations per second passing between platinum electrodes, of solutions of alkali chlorides at $50\text{--}70^{\circ}$, does not take place unless the current density exceeds 100 amperes per sq. cm. Increase of the current density is accompanied by increase of the current yield, which, however, never exceeds 15 per cent., even at a density of 400 amperes per sq. cm. As the electrolysis proceeds, the current yield diminishes, but does not become zero unless the current density is below 250 amperes per sq. cm. The yield is raised and maintained for some time above 10 per cent., if a small quantity of alkali chromate or carbonate is added to the chloride solution. During the formation of chlorate, the platinum electrodes undergo considerable disintegration.

T. H. P.

Behaviour of Potassium Persulphate with certain Salt Solutions. RAFFAELLO PAJETTA (*Gazzetta*, 1906, 36, ii, 298—304).—The solubility of potassium persulphate in water is diminished by the presence of potassium salts and increased by the presence of sodium salts. The author has determined the solubility of the persulphate at 12° in saturated solutions of a number of potassium and sodium salts. The results show that the solubility of potassium persulphate in solutions of sodium salts is a function of their concentration in sodium and that, when the latter is constant for different salt solutions, the solubility of the persulphate is also practically the same in all cases. The potassium persulphate is evidently transformed into the corresponding sodium compound. T. H. P.

Explosion of a Küster Apparatus for the Preparation of Pure Sodium Hydroxide. AUGUST HARPF and HANS FLEISSNER (*Chem. Centr.*, 1906, ii, 994; from *Zeit. chem. Apparatenkunde*, 1, 534—535).—After four days' use a Küster's apparatus (*Abstr.*, 1904, ii, 815) for the preparation of sodium hydroxide from sodium exploded. The explosion was attributed to the ignition of a mixture of hydrogen and oxygen by the heat developed during the reaction between the sodium and the water. By replacing the bell jar by a bottle without a base and drawing off the mixed gases through the neck of the bottle, further explosions were avoided. P. H.

The Explosion of a Küster Apparatus. FRIEDRICH W. KÜSTER (*Chem. Centr.*, 1906, ii, 994—995; from *Zeit. chem. Apparatenkunde*, 1, 535—536. Compare preceding abstract).—The author considers it impossible that the explosion should have been due to oxygen and hydrogen since the apparatus can only have contained pure hydrogen at the time. He attributes the explosion to hydrocarbons produced by sudden contact of a drop of water with sodium carbide and maintains that such sudden contact between liquid and metal is impossible if his instructions are rigidly followed. P. H.

Cæsium Oxide. ÉTIENNE RENGADÉ (*Compt. rend.*, 1906, 143, 592—594).—Cæsium oxide, Cs_2O (compare Beketoff, *Bull. Accad. St. Petersburg*, 1894, iii, 541), can be obtained in a pure state by partially oxidising cæsium with two-thirds the amount of oxygen required to convert the whole of the metal into the oxide, and heating the mixture thus obtained in a vacuum, when the unchanged metal distils at 200°, leaving the oxide Cs_2O in the form of beautiful, orange-red crystals which on heating become red, then purple, and finally black at 150°, and pass through the same colour changes in the reverse order on cooling. Cæsium oxide absorbs moisture and carbon dioxide from the air, reacts energetically and with incandescence with water, melts at 450—500° when heated in a silver boat and is decomposed into the metal and the dioxide; it is similarly decomposed in the presence of liquid ammonia, and the cæsium-ammonium thus formed reacts with the dioxide to form a mixture of cæsamide and cæsium hydroxide (*Abstr.*, 1905, ii, 521). M. A. W.

Action of Oxygen on Cæsium-Ammonium. ÉTIENNE RENGADÉ (*Bull. Soc. chim.*, 1906, [iii], 35, 769—775).—When a solution of cæsium in liquefied ammonia is cooled to -60° and dry oxygen is passed through it, a bulky, white precipitate is first formed, and the blue colour of the liquid disappears. The precipitate then becomes brown in colour and eventually pale yellow. The white precipitate consists of a mixture of cæsium hydroxide, dioxide and amide. The dioxide Cs_2O_2 may be obtained in a pure state by passing a rapid current of dry oxygen through a constantly agitated solution of cæsium in liquefied ammonia. It is a faintly-pink, silky, microcrystalline powder, which fuses to a yellow liquid and resolidifies to a white powder. The brown precipitate consists essentially of *cæsium sesquioxide*, Cs_2O_3 . It is bright brown in colour, may be obtained partially crystalline, melts to a black liquid and when exposed to air rapidly becomes white. The final yellow precipitate is composed of *cæsium peroxide*, Cs_2O_4 . It is bright yellow in colour, melts to a brown liquid and resumes its yellow colour on cooling.

T. A. H.

Hydrolysis of Ammonium Salts. ALEXANDER NAUMANN and ADOLF RÜCKER (*J. pr. Chem.*, 1906, [ii], 74, 249—275).—Solutions of ammonium salts have been distilled, and from the amounts of ammonia in the distillates the hydrolysis has been calculated for each case. This calculation was based on the distillation of dilute solutions of free ammonia, and the determination in this case of the ratio (ammonia in distillate)/(ammonia in distilled solution). These experiments on the distillation of ammonia solutions showed that the partial pressure of the ammonia is not proportional to the concentration of the ammonia solution. The partial pressure of the ammonia falls rapidly as the concentration of the solution diminishes.

To indicate the extent of hydrolysis of various ammonium salts the following numbers may be quoted; they represent the percentage of the ammonia in the solution which is in the free state: $2\text{N}\text{NH}_4\text{Cl}$, 0.03; $2\text{N}\text{NH}_4\text{Br}$, 0.028; $\text{N}(\text{NH}_4)_2\text{SO}_4$, 0.23; $0.5\text{N}(\text{NH}_4)_2\text{C}_2\text{O}_4$, 2.20; $\text{N}\text{H}_2\text{NH}_4\text{PO}_4$, 0.048. The extent of the hydrolysis increases with dilution, but the increase, except in the case of the chloride and bromide, does not coincide with that required by the formula $x^2/(1-x) = K$.

On account of the appreciable hydrolysis of ammonium sulphate, ammonia, especially in dilute solutions, should be titrated with hydrochloric acid, not with sulphuric acid.

J. C. P.

The Hydrolysis of Ammonium Salts in Presence of Iodides and Iodates. SETH E. MOODY (*Amer. J. Sci.*, [iv], 22, 379—382).—Solutions of ammonium chloride or sulphate are slightly dissociated on boiling, but the action is hardly perceptible. If, however, a mixture of potassium iodide and iodate is added, the sulphuric acid is removed as it is liberated, and sets free iodine whilst the ammonia volatilises.

In the author's experiments, 25 c.c. of solution of ammonium sulphate (5 grams per litre) or ammonium chloride (5 grams in 500 c.c.) were introduced into a flask together with the iodate-iodide mixture; no appreciable action takes place in the cold. The solution was boiled in a current of hydrogen until all the iodine liberated had been expelled.

The distillate was passed through a trap containing standard sulphuric acid to absorb the ammonia and then into a Drexel receiver containing potassium iodide to absorb the iodine, which was then titrated as usual with sodium thiosulphate. The results proved that in the circumstances the dissociation of the ammonium salts is almost complete. The chloride is the most easily dissociated salt. L. DE K.

Solubility of Silver Chloride in Hydrochloric Acid and Sodium Chloride Solutions. WILLIAM E. BARLOW (*J. Amer. Chem. Soc.*, 1906, 28, 1446—1449).—Tables are given showing that the solubility of silver chloride in solutions of sodium chloride decreases at a gradually diminishing rate with diminishing concentration, and that the amounts of silver chloride dissolved in hydrochloric acid are directly proportional to the volumes of acid, of fixed concentration, used. In a mixture of sodium chloride and hydrochloric acid, these two act independently.

It is advisable to use nickel crucibles when making determinations of sulphur by fusion with sodium peroxide, as the fused mass obtained in a silver dish contains silver which cannot be removed completely as chloride. L. DE K.

Plaster of Paris. ROBERT DE FORCRAND (*Bull. Soc. chim.*, 1906, [iii], 35, 781—790. Compare van't Hoff and pupils, *Abstr.*, 1900, ii, 531; 1901, ii, 506; 1902, ii, 137; 1904, ii, 35; Rohland, *Abstr.*, 1903, ii, 539, 545; 1904, ii, 33; 1905, ii, 319; Cloez, 1903, ii, 291, 292).—Thomsen's figure, 0.3 Cal., is accepted for the heat of solution of gypsum in water. The semihydrate develops 3.56 Cal. on solution in water at 10°. The anhydrous salt, prepared at 155°, and that obtained by heating this at a red heat for fifteen minutes, develop respectively 5.655 Cal. and 2.92 Cal. on solution in water at 10°. From these and other data (*loc. cit.*), fully discussed in the original, the author concludes that the semihydrate may exist in the three forms $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$, $4\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and $6\text{CaSO}_4 \cdot 3\text{H}_2\text{O}$, whilst gypsum may be represented by $2n\text{CaSO}_4 \cdot 4n\text{H}_2\text{O}$, where $n > 3$. To the anhydrous salt prepared at 155° is assigned the formula 2CaSO_4 , whilst that prepared at a red heat is represented by $2m\text{CaSO}_4$ where probably $m > n$. Le Chatelier's explanation of the setting of plaster of Paris (*Abstr.*, 1883, 712) is regarded as correct, and it is suggested that the non-setting of the anhydrous salt obtained at a red heat is probably due to the fact that it is not convertible into the readily soluble, slightly polymerised semihydrate, whereas this transformation is readily effected by simple hydration in the case of the anhydrous salt prepared at 155°. T. A. H.

Solubility of Calcium Sulphate in Phosphoric Acid Solutions. W. C. TABER (*J. Physical Chem.*, 1906, 10, 626—629). The solubility of calcium sulphate is increased by phosphoric acid, but the curve obtained by plotting the solubility against the concentration of phosphoric acid has a maximum. The maximum value of the solubility observed at 25° was 8 grams per litre, and this is reached when the concentration of the phosphoric acid is 230 grams per litre.

J. C. P.

Solution of Calcium Sulphate in Salt Water. GEORGES ARTH and CRÉTIEN (*Bull. Soc. chim.*, 1906, [iii], 35, 778—781. Compare Abstr., 1904, ii, 30; Cameron, Abstr., 1902, ii, 75; Cloez, Abstr., 1903, ii, 291).—When a saturated solution of sodium chloride is shaken with a mixture of solid sodium chloride and calcium sulphate, the calcium sulphate dissolved, calculated from the amount of calcium oxide in solution, is always different from and greater than that calculated from the sulphuric acid in solution. Similar results are obtained when solid calcium sulphate alone is shaken with a saturated solution of sodium chloride. Tables of the results and curves illustrating these are given in the original. T. A. H.

Preparation of Magnesium and Zinc Peroxides. EMANUEL MERCK (D.R.-P. 171372).—The peroxides of magnesium and zinc as prepared by the ordinary processes of precipitation from alkaline solutions are freed only with some difficulty from the by-products of the double decomposition, and moreover these preparations are not stable in the dried state. It has now been found that when ignited magnesia and dry zinc oxide are treated with a slight excess of chemically pure hydrogen peroxide, substances containing respectively 42 per cent. of magnesium peroxide and 61 per cent. of zinc peroxide are obtained. G. T. M.

Nitrides of Zinc, Aluminium, and Iron. ALFRED H. WHITE and L. KIRSCHBRAUN (*J. Amer. Chem. Soc.*, 1906, 28, 1343—1350).—When zinc dust is treated with dry ammonia at 600°, zinc nitride is produced, but since the compound begins to decompose below 600° it is not possible in this way to obtain a nitride of theoretical composition. The highest percentage of nitrogen found in any sample thus prepared was 10·6 (Zn_3N_2 requires $\text{N}=12\cdot5$ per cent.), and the product is regarded as a mixture or solid solution of zinc nitride and zinc. The properties of this substance are identical with those of the nitride, Zn_3N_2 , obtained by Frankland (*Phil. Mag.*, 1858, [iv], 15, 149) by the action of heat on zincamide.

By the action of dry ammonia on powdered aluminium at 700° a product is obtained containing a small quantity (up to 1·8 per cent.) of nitrogen. The nitride is decomposed by boiling water with formation of ammonia.

Ammonia reacts with spongy iron, which has been reduced with hydrogen, with formation of the nitride. The most favourable temperature is 450—475°, but the product always contains less nitrogen than is required by the formula Fe_3N_2 . Preparations containing 10 per cent. of nitrogen are scarcely appreciably attacked by neutral potassium copper chloride solution, and although slowly attacked by an acid solution of this salt do not suffer any change in their percentage composition. The products are therefore considered to be solid solutions of iron nitride in iron (compare Braune, Abstr., 1905, ii, 638). E. G.

Double Chlorides of Lead and Potassium. RICHARD LORENZ and W. RUCKSTUHL (*Zeit. anorg. Chem.*, 1906, 51, 71—80).—The

freezing point curve of the system shows a flat maximum at 430° and 33.3 mol. per cent. of potassium chloride corresponding with the compound $2\text{PbCl}_2, \text{KCl}$, and two breaks at 440° and 60 mol. per cent. and 480° and 68 mol. per cent. of potassium chloride respectively, indicating the existence of two other compounds, the compositions of which, as shown by thermal analysis, are $\text{PbCl}_2, 2\text{KCl}$ and $\text{PbCl}_2, 4\text{KCl}$ respectively. The latter decomposes above 480° into solid potassium chloride and a fused mass corresponding in composition with the break in the curve at 480° ; the former decomposes above 440° into solid $\text{PbCl}_2, 4\text{KCl}$ and a fused mass corresponding in composition with the break in the curve at that temperature. The compound $2\text{PbCl}_2, \text{KCl}$ forms two series of mixed crystals from 31.7—33.3 and 33.3—34.1 mol. per cent. of potassium chloride respectively. There are two eutectic points, at 410° and 20 mol. per cent. and 405° and 50 mol. per cent. of potassium chloride respectively.

The compound $2\text{PbCl}_2, \text{KCl}$ forms an almost transparent, glassy mass; $\text{PbCl}_2, 2\text{KCl}$ occurs in long, well-defined rhombic crystals, and $\text{PbCl}_2, 4\text{KCl}$ in reddish-white, granular masses. G. S.

Electrolytic Preparation of Lead Peroxide from Lead Sulphide. FRIEDRICH R. STEIGELMANN (D.R.-P. 162107).—When natural or artificial lead sulphide is made the anode in an electrolytic cell, water containing a small quantity of an acid, alkali, or salt being used as electrolyte, lead peroxide and sulphuric acid are formed according to the equation $\text{PbS} + \text{H}_2\text{O} + 50 = \text{PbO}_2 + \text{H}_2\text{SO}_4$. The quantity of acid initially added must not exceed 1 per cent., or hydrogen sulphide is evolved. When the reaction has once started, the layer of lead peroxide formed protects the sulphide from the action of the sulphuric acid produced in the reaction. C. H. D.

Identification of Solid Phases. L. F. HAWLEY (*J. Physical Chem.*, 1906, 10, 654—657).—Mixtures of lead oxide and carbonate in varying proportions were left for twelve to fourteen hours in contact with 20 per cent. sodium acetate solutions at 75° . Both the solutions and the solid phases were then analysed. It appears that no solid solutions are formed between lead oxide and lead carbonate, and that white lead is a definite compound of two molecules of the carbonate and one of the hydroxide.

The relations of thallium sulphide and stannic sulphide were studied under the microscope. The solid phases occurring in this system are thallium sulphide, the compound, Tl_4SnS_4 , and solid solutions lying between 76 and 100 molecular per cent. of stannic sulphide.

J. C. P.

Action of Strong Sulphuric Acid on Copper. CHARLES M. VAN DEVENTER (*Chem. Centr.*, 1906, ii, 1107—1108; from *Chem. Weekblad*, 1906, 3, 515—519).—The author has modified his former view (Abstr., 1905, ii, 383) with regard to the action of strong sulphuric acid on copper, and considers that neither the reduction nor the oxidation theories are satisfactory. It is suggested as an alternative that water plays an important part in the reaction: $\text{Cu} + \text{H}_2\text{O} = \text{CuO} + 2\text{H}$;

$\text{CuO} + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{H}_2\text{O}$; and $2\text{H} + \text{H}_2\text{SO}_4 = 2\text{H}_2\text{O} + \text{SO}_2$. This theory explains how it is possible for ammonia to be formed during a process of oxidation such as occurs in the Kjeldahl method of estimating nitrogen. P. H.

Copper and Phosphorus. E. HEYN and O. BAUER (*Mitt. k. Materialprüfungs-Amt.*, 1906, 24, 93—109).—The freezing-point curve of the copper-phosphorus alloys has been determined for the range 0—15 per cent. of phosphorus, and consists of two branches, meeting at an eutectic point at 707° and 8.27 per cent. of phosphorus. There is a maximum at 14.09 per cent. of phosphorus, corresponding with the compound, Cu_3P , which melts at 1024° . Copper is able to retain 0.175 per cent. of phosphorus in solid solution; alloys containing more than this show the presence of an eutectic. The curves representing the specific gravity and the electromotive force of the alloys show a break only at the composition of the phosphide, Cu_3P . Measurements of the area of crystals and eutectic in the micro-photographs were made by means of a planimeter, but the copper areas were found to be larger than calculation from the composition would indicate.

The copper-phosphorus alloys are harder than the copper-tin alloys, and the compound Cu_3P is harder than Cu_3Sn .

It is not possible to prepare alloys containing more than 15 per cent. of phosphorus by fusion, but at $300\text{--}400^\circ$ copper combines with as much as 27 per cent. of phosphorus, a part of which is evolved on heating, until at 1100° not more than 14.09 per cent. is retained. By very rapid fusion of such rich mixtures, supersaturated alloys can be obtained, and are found to contain mixed crystals of Cu_3P and a higher phosphide. A diagram is given of the probable conditions of equilibrium with the vapour phase.

The paper is illustrated with micro-photographs.

C. H. D.

Researches on the Rare Earths. II. GEORGES URBAIN (*J. Chim. phys.*, 1206, 4, 321—357. Compare this vol., ii, 449, 510, 674).—An epitome of work already published.

H. M. D.

Atomic Weight of Dysprosium. GEORGES URBAIN and M. DEMENITROUX (*Compt. rend.*, 1906, 143, 598—600. Compare this vol., ii, 359, 674).—Dysprosium sulphate, $\text{Dy}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, forms brilliant crystals slightly yellow in colour; it is stable at 110° , and completely dehydrated at 360° , and the anhydrous salt is converted into the oxide at a white heat. The atomic weight of dysprosium, determined from the ratio $\text{Dy}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O} : \text{Dy}_2\text{O}_3$ was 162.52 (six determinations) with the limits 162.29 and 162.75, when the dysprosium earth was isolated by fractional crystallisation of the nitrate; and 162.54 (six determinations) with the limits 162.36 and 162.63 in the case of compounds obtained by fractional crystallisation of the ethyl sulphates [$\text{O} = 16$, $\text{H} = 1.007$, $\text{S} = 32.06$]. M. A. W.

The System: Water, Lithium Sulphate, and Aluminium Sulphate. FRANS A. H. SCHREINEMAKERS and A. J. C. DE WAAL (*Chem. Centr.*, 1906, ii, 1165—1166; from *Chem. Weekblad.* 1906, 3, 539—543).—The results obtained by the study of the equilibria of

the above system at 30° are recorded in tabular and graphic form. In accordance with theory, it was found that when an unsaturated solution containing equivalent quantities of lithium and aluminium sulphates is evaporated at a constant temperature, crystals of aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, separate. Although no evidence of a lithium alum could be obtained, it is suggested that this substance may perhaps only be stable at temperatures below 30°. P. H.

Solubility of Potassium Permanganate. GREGORY P. BAXTER, ARTHUR C. BOYLSTON, and ROBERT A. HUBBARD (*J. Amer. Chem. Soc.*, 1906, 28, 1336—1343).—Determinations of the solubility of potassium permanganate in water at various temperatures have been made by rotating tubes containing the salt and water in a thermostat maintained at the required temperature and subsequently analysing the saturated solutions. The method and apparatus employed are fully described with the aid of a diagram. The results are tabulated and plotted as a curve.

The following solubilities are in each case the average of several determinations, and are expressed as parts by weight of potassium permanganate in 100 parts by weight of the solution: at 0°, 2.754; at 9.8°, 4.133; at 19.8°, 5.958; at 24.8°, 7.055; at 29.8°, 8.283; at 34.8°, 9.643; at 40°, 11.155; at 45°, 12.728; at 50°, 14.446; at 55°, 16.201; at 65°, 20.021. The following are the solubilities expressed as parts of potassium permanganate dissolved in 100 parts of water: at 0°, 2.83; at 9.8°, 4.31; at 19.8°, 6.34; at 24.8°, 7.59; at 29.8°, 9.03; at 34.8°, 10.67; at 40°, 12.56; at 45°, 14.58; at 50°, 16.89; at 55°, 19.33; at 65°, 25.03. E. G.

Electrolytic Deposition of Iron from Aqueous Solutions of its Chloride and Sulphate. A. RYSS and A. BOGOMOLNY (*Zeit. Elektrochem.*, 1906, 12, 697—703).—With solutions of ferrous chloride the current density at the cathode should not exceed 0.004 ampere per sq. cm. Rapid rotation of the cathode improves the quality of the deposit. A solution containing equal weights of ferrous chloride and water at a temperature of 60—70° gives the best result. Up to 0.3 mm. thickness the deposits are perfect. With solutions of ferrous ammonium sulphate the best conditions are: maximum current density, 0.005 ampere per sq. cm.; concentration, 70 grams of the crystallised salt per litre; temperature, 15—18°. The deposits are good up to a thickness of 1.2 mm. The effects of adding some twenty-four different substances to the solutions were studied, but no improvement in the deposit was observed.

From the bath proposed by Maximowitsch (*Abstr.*, 1905, ii, 253) it is possible to obtain a homogeneous deposit of iron of any thickness. The best conditions are: current density at the (rotating) cathode, 0.003 ampere per sq. cm.; solution, 200 grams of ferrous chloride (or ferrous ammonium sulphate), 50 grams of magnesium sulphate and 5 grams of sodium hydrogen carbonate per litre of water; temperature, 15—18°. During the electrolysis 4 or 5 grams of sodium hydrogen carbonate per litre of electrolyte are added at intervals of three days. Special experiments showed that both the magnesium

sulphate and the sodium hydrogen carbonate are essential constituents of the bath. T. E.

Nature of Pseudo-solutions of Ferric Hydroxide. I. FEDERICO GIOLITTI (*Gazzetta*, 1906, 36, ii, 157—167. Compare Abstr., 1905, ii, 823).—Gelatinous ferric hydroxide, obtained by adding excess of ammonia to a solution of a ferric salt, dissolves to a slight extent when washed with pure water, giving a colloidal solution. If the thoroughly washed precipitate is kept in pure water for three or four months, dark nuclei develop which have a diameter of about 7μ and remain undissolved when the mass is treated with acetic acid. If the opaque, opalescent liquid thus obtained with acetic acid is either kept or centrifugated part of the dissolved matter separates in the form of these nuclei, and a pseudo-solution is also obtained with which small proportions of binary electrolytes yield no precipitate, whilst larger proportions give soluble, and multivalent electrolytes insoluble, precipitates; the solution is, indeed, identical in properties with that prepared by long boiling of ferric acetate (Péan de Saint-Gilles). The formation of nuclei is also observed when the well-washed hydroxide is boiled with water for twenty-four to thirty-six hours, the high temperature favouring the change.

In the case of ferric hydroxide which has been suspended for some time in acetic acid, definite limits of stability (*loc. cit.*) towards nitric acid exist, but, if the hydroxide or acetate is boiled with water, the limit of stability varies with the duration of the boiling; there is, doubtless, a relation between the limit of stability and the magnitude of the particles.

Similar results are observed with the pseudo-solution obtained by treating sodium tungstate solution with excess of hydrochloric acid and subsequently removing all the electrolyte by washing.

Examination of the absorption spectra of solutions of ferric hydroxide prepared in various ways shows that these possess quite different colours.

The author discusses the various views held as to the constitution of ferric hydroxides, and concludes that the existence of basic salts is highly improbable. The action of acid only serves to separate the ready-formed nuclei from the non-modified residue. T. H. P.

Nature of Pseudo-solutions of Ferric Hydroxide. II. FEDERICO GIOLITTI and BATTISTI (*Gazzetta*, 1906, 36, ii, 433—443).—The authors have determined the limits of stability of various pseudo-solutions of ferric hydroxide with respect to certain electrolytes, more especially nitric acid. The results show that these limits of stability are not merely a function of the dimensions of the particles constituting the solution, but that they depend also on certain specific causes connected with true chemical actions of the electrolyte on the suspended particles (compare Spring, Abstr., 1900, ii, 713). T. H. P.

Properties of Barium Ferrate. A. BASCHIERI (*Gazzetta*, 1906, 36, ii, 282—286).—Barium ferrate is practically not decomposed by dilute sulphuric acid in the cold, but the decomposition increases as

the temperature rises until it becomes complete in the boiling acid. Dilute hydrochloric (sp. gr. 1.09) or nitric acid, however, decomposes barium ferrate almost instantaneously with formation of salts of iron and barium, and in the case of the former acid with evolution of chlorine. When the ferrate is treated in the cold with a more dilute hydrochloric acid, vigorous evolution of chlorine takes place, the precipitate gradually disappears, and the solution assumes a vermilion colour; this liquid continues to evolve chlorine for about a day and slowly turns colourless. The vermilion colour of the solution is due, not to the intermediate formation of a chloroferrate, but to the presence of the ion FeO_4^{2-} .

Barium ferrate dissolves also in solutions of organic acids, the solubility and the intensity of colour imparted to the liquid increasing as the acid becomes more energetic.

T. H. P.

Distribution of Nickel and Cobalt in Nature. KARL KRAUT (*Zeit. angew. Chem.*, 1906, 19, 1793—1795).—The author has found traces of nickel by means of Tschugaeff's dimethylglyoxime method (*Abstr.*, 1905, ii, 613) in a variety of peats and coals. Cobalt occurring together with nickel can be detected in the ammoniacal filtrate from the nickeloximine by allowing the solution to remain in a closed glass vessel for some time with a small quantity of hydrogen, ammonium, or sodium sulphide, when a bluish-violet or claret-red colour is developed.

P. H.

Atomic Weight of Cobalt. IV. Analysis of Cobaltous Chloride. GREGORY P. BAXTER and FLETCHER B. COFFIN (*Zeit. anorg. Chem.*, 1906, 51, 171—180. Compare *Abstr.*, 1898, ii, 377; 1899, ii, 753; 1900, ii, 78).—The chloride employed in the present series of experiments was much purer than that formerly used, as the purification has now been carried out in vessels of quartz. One sample was purified by conversion into the purpureo-chloride; the latter was dissolved in ammonia and the ammine crystallised three times, then heated for some time below its melting point in air, and finally in a current of hydrogen chloride to remove water and ammonium chloride. Another portion of the ammine was converted into sulphate, treated with excess of ammonia, the metal precipitated by electrolysis, dissolved in hydrochloric acid, and the chloride recrystallised and dehydrated by heating carefully below its melting point.

For the atomic weight determination, the sample, before weighing, was dried at 400° in a stream of hydrogen chloride and then in a mixture of hydrogen chloride and nitrogen, precipitated with the exactly equivalent quantity of silver dissolved in nitric acid, the end point being determined by means of the nephelometer; finally, the silver chloride was collected and weighed.

A series of eight concordant determinations from the ratio $\text{CoCl}_2 : 2\text{Ag}$, and another of seven determinations from the ratio $\text{CoCl}_2 : 2\text{AgCl}$, both gave a mean value of 58.997 for the atomic weight of cobalt, in excellent agreement with the value, 58.995, previously obtained by analysis of the bromide ($\text{Cl} = 35.473$; $\text{Ag} = 107.93$).

G. S.

Composition of Acid Chloropentamminecobaltsulphate.

HEINRICH BILTZ and ERNST ALEFELD (*Ber.*, 1906, 39, 3371—3372).—The hydrogen sulphate of the chloropentamminecobalti series described by Jörgensen (*Abstr.*, 1879, 119, 597) is expressed by the formula $[(\text{CoCl}(\text{NH}_3)_5)\text{SO}_4\text{H}]_2\text{SO}_4$. The salt is not precipitated by silver nitrate in the cold, and only slowly and incompletely after prolonged boiling. E. F. A.

Action of Hydrazine Hydrate on Complex Cobalt Salts.

HARTWIG FRANZEN and O. VON MAYER (*Ber.*, 1906, 39, 3377—3380).—*Dihydrazinecobaltchloride*, $\text{CoCl}_2(\text{N}_2\text{H}_4)_2$, prepared either by the action of hydrazine on chloropentamminecobaltchloride, on chloro-aquopentamminecobaltchloride, or on hexamminecobaltchloride, is a rose-coloured powder which decomposes to a green powder on boiling with water. *Dihydrazinecobaltbromide* is obtained either as a violet powder or in brownish-red crystals, which are decomposed by water. *Dihydrazinecobalto-oxalate*, $\text{CoC}_2\text{O}_4(\text{N}_2\text{H}_4)_2$, is a raspberry-red, coarse, crystalline powder composed of short, thick columns; it is not decomposed on heating with water. *Trihydrazinecobaltosulphate*, $\text{CoSO}_4(\text{N}_2\text{H}_4)_3$, is a loam-yellow, crystalline powder, which decomposes when boiled with water forming a green powder. E. F. A.

Equilibrium and Transformations of the Isomeric Hydrates of Chromium Chloride. J. OLIE, jun. (*Zeit. anorg. Chem.*, 1906, 51, 29—80. Compare *Abstr.*, 1905, ii, 716).—The paper contains a more detailed account of work already published, with some additional observations. Whilst some weeks elapse before the green and violet modifications of chromic chloride attain equilibrium in solution at 25°, this is effected within forty-eight hours at 84°; in solutions containing 0 to 70 per cent. of salt, the equilibrium is displaced towards the green modification at the latter temperature as compared with 25°. Hydrogen chloride retards the attainment of equilibrium and displaces it towards the green salt. At 84—100°, the equilibrium mixture (in the absence of water) contains about 36 per cent. of the violet form.

The investigation of the freezing-point curve of the system is rendered difficult owing to the fact that it has been found impossible to bring the green form to crystallisation under definite conditions, even in the presence of its own crystals. The green salt melts at 83.5°, but it is considered that in this case partial transformation has taken place, and that the true melting point of this form is a little above 90°. The violet form melts with partial transformation at 95°. The eutectic temperature lies at 73°, and the mixture contains the two salts in approximately equivalent proportions.

The green modification is the only stable solid phase from 0° to its melting point. G. S.

Chromium Dioxide and the Constitution of Chromium Trioxide. WILHELM MANCHOT and R. KRAUS (*Ber.*, 1906, 39, 3512—3515).—*Chromium dioxide*, CrO_2 , when prepared by heating chromic hydroxide in a current of oxygen at 320—345° for several

hours, forms a light, hygroscopic, black powder containing 6—7 per cent. of water which is evolved together with the peroxide oxygen on heating the substance at a red heat, leaving a residue of green chromic oxide. The dioxide is only slowly decomposed by hydrochloric or hydriodic acid. Nitric acid dissolves it, forming chromic acid. When treated with water alone, the dioxide yields no chromic acid, but the addition of alkali brings about this result, which is due to simultaneous oxidation and reduction of the dioxide. Sulphuric acid is produced by the interaction of warm sulphurous acid and the dioxide. The compound has the colour and properties of a peroxide and not of a chromic chromate, and is probably $\text{O}:\text{Cr}:\text{O}$. It thus differs from the peroxide, $\text{O}:\text{Cr}:\text{O}:\text{O}:\text{Cr}:\text{O}$, which appears as the primary product of the autoxidation of chromous oxide. The existence of this chromium dioxide is regarded as evidence in favour of the view that chromium is quadri-valent in chromium trioxide (compare this vol., ii, 364). G. T. M.

Solubility and Solution Equilibrium of Chrome Ammonium Alum. IWAN KOPPEL (*Ber.*, 1906, 39, 3738—3748. Compare Roozeboom and Olie, *Abstr.*, 1905, ii, 716; Roozeboom and Aten, *ibid.*, 803).—The change of the violet into the green chromium salt solutions is a reversible process which results in the slow formation of an equilibrium depending on the temperature; during the change, the normal dissociated anions combine with the chromium to form the green complex substance, the formation of which is accompanied usually by a parallel hydrolysis. The equilibrium between a solute and its saturated solution is soon established if the solute undergoes no change or if its rate of change is greater than its rate of solution; but if the rates of change and solution are equal, or if the rate of change is smaller than that of solution, the solution apparently becomes saturated and then slowly increases in concentration. The appearance of a final concentration value shows the formation of an equilibrium between the solute and its product of change, whilst the rate of change may be deduced from the rate of solution after the primary saturation. These points are illustrated by tables and curves for the rates of solution of chrome ammonium alum at 30° and 40°. No change of the violet into the green solution takes place at 0°, the solubility of chrome ammonium alum in water not increasing between 2 hours 30 minutes and 214 hours 15 minutes. From these experiments, it is calculated that when in equilibrium the solution of chrome ammonium alum at 30° contains 33 per cent., or at 40°, 37.5 per cent. of the green alum; the values obtained are discussed and held to be only approximate.

Electrolytic conductivity measurements with green and violet solutions containing 3.80 grams of the alum per 100 grams of the solution and with mixtures of these, gave results agreeing with the presence of 48 per cent. of the green complex at 40° and 61 per cent. at 55°.

The proportion of the green complex present when the solution is in equilibrium decreases, and, after passing through a minimum, again increases as the solution is diluted. G. Y.

Preparation of Fused Molybdenum. HEINRICH BILTZ and RICHARD GÄRTNER (*Ber.*, 1906, 39, 3370—3371).—Fused molybdenum

is obtained very conveniently from a mixture of molybdenum dioxide prepared by the reduction of the trioxide in a stream of hydrogen, or by ignition of ammonium molybdate, and aluminium powder, the reaction being started in the ordinary way. E. F. A.

Pure Alloys of Tungsten and Manganese, Preparation of Tungsten. G. ARRIVAUT (*Compt. rend.*, 1906, 143, 594—596).—Tungsten-manganese alloys, containing 12.21 to 60.05 per cent. of tungsten, obtained by reducing with aluminium a mixture of the oxides of the two metals with their respective peroxides, form hard, brittle ingots, steel-grey in colour, and non-magnetic.

These alloys, which do not contain any definite compounds of the two metals, are slowly oxidised in the air, and completely dissolved by boiling concentrated sulphuric acid or by fused alkali hydrogen sulphates; dilute acids attack them in the cold, dissolving the manganese and leaving the tungsten in the form of a heavy, metallic, steel-grey powder having a sp. gr. 15.28 at 0°, the sp. gr. of the fused metal being 18.7 (Moissan, Abstr., 1896, ii, 606).

Alloys of tungsten and manganese, containing not more than 25 per cent. of the former metal, can be also prepared by fusing a mixture of the metallic powders in a current of hydrogen (compare this vol., ii, 676, 758). M. A. W.

Equilibrium Phenomena with the Hydrates of Uranous Sulphate. III. The Hexahydrate, Pentahydrate, and Basic Sulphates. FEDERICO GIOLITTI and G. LIBERI (*Gazzetta*, 1906, 36, ii, 443—450. Compare Abstr., 1905, ii, 827).—By the interaction of uranyl sulphate, water, alcohol and sulphuric acid in various proportions, the following salts have been isolated: (1) $U(SO_4)_2 \cdot 6H_2O$, in mammillary masses of small, pale green crystals; (2) $U(SO_4)_2 \cdot 5H_2O$, as a pale green incrustation; (3) $U(SO_4)_2 \cdot 8H_2O$, in stellar aggregates of green, acicular crystals; (4) $3UOSO_4 \cdot U(SO_4)_2 \cdot 32H_2O$, as a pale green powder, which, on drying in the air, yields (5) $3UOSO_4 \cdot U(SO_4)_2 \cdot 10H_2O$; (6) $3UOSO_4 \cdot U(SO_4)_2 \cdot 20H_2O$; (7) $3UOSO_4 \cdot U(SO_4)_2 \cdot 15H_2O$, and (8) $UOSO_4 \cdot 5H_2O$.

Many of the phenomena presented by the uranous sulphates are almost certain indications that, in these salts, the sulphuric acid residue does not form ions by itself, but constitutes part of certain complex ions, which contain also uranium. This would explain the large number of different salts obtained, the complexity of their formulæ, and the fact that uranous sulphates of identical composition often exhibit divergent crystalline forms and other physical and chemical properties. T. H. P.

Constitution of the Copper-Tin Alloys. EARNEST S. SHEPHERD and E. BLOUGH (*J. Physical Chem.*, 1906, 10, 630—653. Compare Abstr., 1905, ii, 587; Heycock and Neville, Abstr., 1901, ii, 508; 1902, ii, 261).—The method suggested by Bancroft (Abstr., 1902, ii, 495) has been used to determine the composition of the six solid phases which coexist with fused mixtures of copper and tin varying in

composition between the pure metals. It is found that the phases are α , β , γ , and ϵ , all solid solutions, the compound Cu_3Sn , and pure tin. A microscopic study of the solid alloys has been made and all the results are incorporated in a temperature concentration diagram, worked out for temperatures above 219° . It appears that below 600° the δ -solid solution can exist; this phase was supposed previously to be the compound Cu_4Sn . Mixtures of the compound Cu_3Sn and the ϵ -crystals show heat effects at 218° and 182° , but the nature of these changes is still in doubt. J. C. P.

Electrolytic Precipitation of Bronzes. B. E. CURRY (*J. Physical Chem.*, 1906, 10, 515—520).—The general method for preparing bronze plate is to precipitate a brass and bronze it by chemical methods. The author finds that with a rotating cathode and acid ammonium oxalate solutions good bronze may be precipitated. The percentage of copper in the metal deposited differs widely from that in the solution, falling from 100 to 77, when that in the solution falls from 100 to 20; and it is difficult to obtain a good deposit with less than 75 per cent. of copper. The cathode current density should be low; good deposits were obtained with densities of 0.2 to 2.0 amperes per square decimetre. The deposited bronzes correspond closely in appearance with cast bronzes of the same composition. L. M. J.

Treatment of Uranium-Vanadium Metals and the Electrolytic Preparation of Vanadium. M. GIN (*Chem. Centr.*, 1906, ii, 1172—1173; from *Elektrochem. Zeit.*, 1906, 13, 119—122).—Carnotite is decomposed by fusion with potassium hydrogen sulphate. After solution in water, concentration, and cooling, the uranium and vanadium separate as the double potassium sulphate. On treatment with zinc the vanadium is reduced and is then precipitated by neutralisation with ammonia and addition of ammonium carbonate; the uranium is obtained on boiling the filtrate. Another method is based on heating to redness in the vapour of ferric chloride, when vanadyl chloride, VOCl_3 , which is readily volatile, is formed.

An outline is given of the preparation of vanadium by the electrolysis of the oxide V_2O_5 , which conducts well, but the precise details of the process are not described. P. H.

Hydrogen Aurichloride. ERNST SCHMIDT (*Chem. Centr.*, 1906, ii, 855—856; from *Apoth. Zeit.*, 21, 661—662).—Hydrogen aurichloride crystallises with $3\text{H}_2\text{O}$ as stated by Weber (*Jahresber.*, 1867, 314) and by Schottländer (Abstr., 1883, 853), and not with $4\text{H}_2\text{O}$ as stated by Thomsen (Abstr., 1878, 13; 1883, 1054). P. H.

Some Catalytic Actions of Platinum Black. OSCAR LOEW and KEIJIRO ASO (*Bul. Coll. Agr. Tōkyō, Imp. Univ.*, 1906, 7, 1—6. Compare Abstr., 1890, 453 and 689).—Platinum black has the power of converting maleic acid into fumaric acid. In presence of dextrose it reduces free nitric acid to ammonia, and potassium chlorate, per-

chlorate and iodate to chlorides and iodide. It also has a reducing action on nitrobenzoic acid and trinitrophenol.

When kept moistened with water for some time, platinum black is found to contain nitric acid and traces of ammonia. N. H. J. M.

Mineralogical Chemistry.

Natural and Artificial Coloration of Amethyst, &c. MARCELLIN BERTHELOT (*Compt. rend.*, 1906, 143, 477—488).—Small crystals of amethyst from Brazil, when heated to 300°, became decolorised. The loss of colour is supposed to be due to the reduction of traces of manganic to manganous salts, with the occlusion of oxygen in the stone. On exposing the decolorised crystals to the action of radium chloride, contained in a sealed glass tube, the original colour is regained in the course of a few weeks, owing to the reoxidation of the manganese salt. Similar results were obtained with violet fluorspar. Fused quartz and glass, containing traces of manganese, also acquired a violet tint when exposed to the action of radium chloride in the same manner; paper also showed signs of oxidation. It is suggested that the colour of amethyst, and possibly of some other precious stones, may be due to the action of radioactive substances while the stones lie buried in the earth's crust. The decolorisation by heat of smoky quartz and green fluorspar is accompanied by the distillation of petroleum, and in these cases the colour must be due to organic matter (compare Abstr., 1901, ii, 166).

L. J. S.

Blue Rock Salt. ERNST PIESZCZEK (*Chem. Centr.*, 1906, ii, 906; from *Pharm. Zeit.*, 51, 700—701).—The blue portions of rock salt were found to contain 0·4 per cent. less chlorine than pure sodium chloride or than the blue portions rendered colourless by heating. The excess of sodium is attributed to the presence of a subchloride rather than to the presence of metallic sodium as suggested by Siedentopf (this vol., ii, 443) or by Stähli (*Apoth. Zeit.*, 1906, 21, 203), inasmuch as the colour is not removed by boiling with alcohol or by heating at 100° in a sealed tube with mercury.

P. H.

Formation of Oceanic Salt Deposits. XLIX. Artificial Production of Colemanite. JACOBUS H. VAN'T HOFF (*Sitzungsber. K. Akad. Wiss. Berlin*, 1906, 39, 689—693. Compare this vol., ii, 619).—It is found that boronatrocalcite not only yields pandermite when heated with a solution saturated with sodium and potassium chlorides at its boiling point (110°), but that the same change takes place in presence of excess of water at very much lower temperatures. The reaction proceeds, moreover, much more readily in porcelain than in glass vessels.

From boronatrocalcite and water in the proportion 1 : 40 the heptahydrate, $2\text{CaO}, 3\text{B}_2\text{O}_3, 7\text{H}_2\text{O}$, was obtained at 90° and the enneahydrate, $2\text{CaO}, 3\text{B}_2\text{O}_3, 9\text{H}_2\text{O}$, at 60° , when the solution was nucleated with crystals of the respective hydrates. At 83° (the higher limit of the investigation), colemanite, $2\text{CaO}, 3\text{B}_2\text{O}_3, 5\text{H}_2\text{O}$, is the stable form of dicalciumtriborate in contact with a solution saturated with sodium chloride. The transformation of the heptahydrate into colemanite, which is accompanied by a diminution in volume, takes place at 40° in presence of sodium chloride, whilst in presence of a solution saturated with sodium chloride, potassium chloride, and glaserite (which has the lowest vapour pressure of all solutions capable of yielding calcium borates), the change takes place below 25° . Colemanite is therefore one of the Stassfurt salts which may have been formed at a temperature below 25° .

H. M. D.

The Amount and Origin of the Ammonia in the Products of the Eruption of Vesuvius in April, 1906. JULIUS STOKLASA (*Ber.*, 1906, 39, 3530—3537).—Contrary to the statements made by other observers that the ammonium chloride found on the lower portions of the lava outflow was due to the burning of vegetation, the author has found ammonium chloride on large blocks of lava at an altitude of 900 metres in places where no vegetation was present, and even in the sand of the crater. The gases streaming out of the crater on May 4th, 1906, contained hydrogen chloride and ammonia, and the whitish-yellow smoke which accompanied the eruption consisted principally of ammonium compounds. In certain localities there were in the lava white druses containing ammonium chloride mixed with the chlorides and sulphates of sodium and potassium. Some of the druses were coloured yellow by ferric chloride, and others exhibited a green colour due to copper chloride.

The portions of lava soluble in water often contained as much as 76—85 per cent. of ammonium chloride. In the lapillæ, the water-soluble portions yielded 33 per cent. of ammonium chloride. The red ash contained only 0.1 per cent. of ammonia, and traces merely were found in the grey ash. All the products of the eruption when heated to redness with soda-lime evolve ammonia, the largest amounts being obtained from a specimen of lapillæ and an olivine bomb. This result points to the existence of various nitrides which would in these circumstances evolve ammonia.

G. T. M.

Breunnerite from Avigliana. GIUSEPPE PIOLTI (*Atti R. Accad. Torino*, 1906, 41, 1066—1069).—A sample of breunnerite obtained from a serpentine cave near Avigliana was found to have n_D 1.715, and the percentage composition: MgCO_3 , 90.47; FeCO_3 , 9.45; MnCO_3 , traces. The angle of the cleavage rhombohedron had the value $107^\circ 30'18''$.

T. H. P.

Analysis of the Ash which fell in Naples on the Night of April 4—5th, 1906. EZIO COMANDUCCI and M. ARENA (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 267—280. Compare Comanducci and Pescitelli, this vol., ii, 177; Johnssen, this vol., ii,

621; Oglialoro, this vol., ii, 621).—Analysis of the ash which was emitted from Vesuvius and collected in Naples on the night between April 4th and 5th gives the following percentages:

Cl.	SO ₃ .	P ₂ O ₅ .	SiO ₂ .	TiO ₂ .	Fe ₂ O ₃ .	FeO.
0.5992	0.9361	0.7494	43.6865	0.1720	12.2915	2.7219
MnO.	Al ₂ O ₃ .	MgO.	CaO.	CoO.	CuO.	K ₂ O.
0.2962	16.7468	2.2982	11.9677	0.0038	0.0854	4.6609
	Na ₂ O.	NH ₃ .	NO ₂ .	NO ₃ .	SO ₂ .	
	4.6329	0.03071	0.00134	0.000054	0.0224.	

Fragments of crystals of leucite, felspar, augite, magnetite, and ferrite were detected in the ash. T. H. P.

Silicate Fusions. HANS HERIBERT REITER (*Jahrb. Min.*, 1906, *Beil.-Bd.*, 22, 183—265).—A continuation of the work of C. Doelter on silicate fusions; the results obtained are discussed in detail with respect to the views expressed by Doelter and Vogt (*Ann. Rep.*, 1904, 1, 224; 1905, 2, 269). In the several experiments various minerals (albite, nephelite, augite, olivine, and magnetite) were fused together in different proportions. The order of separation of the minerals in the crystallised products so obtained is: spinel, hæmatite, magnetite, olivine, magnetite, augite, magnetite, nephelite, plagioclase. The fact that spinel is formed as a new component of these mixtures proves that there must have been dissociation, and the recurrence of magnetite shows that the order of separation does not depend on the fusibility of the minerals, but rather on the varying saturation of the silicate solution. L. J. S.

Compounds Allied to Spinel. Z. WEYBERG (*Centr. Min.*, 1906, 645—649).—Attempts to produce alumino-, chromi-, and ferri-silicates of the type $R''R_2'''Si_2O_8$ by fusing the materials with salts of alkalis or alkaline earths (*Abstr.*, 1906, ii, 23, 91) have frequently resulted in the formation of double oxides of the spinel type, $R''R_2'''O_4$. Silicic acid, aluminium hydroxide, and lithium carbonate, in the proportions given by $2SiO_2$, Al_2O_3 , Li_2O , when fused for several hours with an excess of lithium sulphate gave a white powder consisting of rounded, birefringent (perhaps orthorhombic) grains of lithium aluminate, $Li_2Al_2O_4$. Lithium chromite, $Li_2Cr_2O_4$, was obtained by fusing kaolin with lithium chromate; it crystallises as brown, isotropic octahedra with the characters of a spinel. When this crystallised lithium chromite is fused, it produces chromic oxide in crystals of an unusual habit. Calcium chromite, $CaCr_2O_4$, was obtained as green, strongly pleochroic, acicular crystals by fusing kaolin with potassium chromate and calcium oxide. Several attempts to synthesise the ferrisilicates resulted in the formation of violet-black octahedra with the composition $2CaO, 5Fe_2O_3$. L. J. S.

Minerals of the Composition $MgSiO_3$; a Case of Tetramorphism. EUGENE T. ALLEN, FRED. EUGENE WRIGHT, and J. K. CLEMENT (*Amer. J. Sci.*, 1906, [iv], 22, 385—438).—The orthorhombic

and monoclinic amphiboles and pyroxenes with the composition MgSiO_3 have all been prepared artificially, some of them for the first time. They were usually obtained as spherulites or finely fibrous aggregates and were identified by their optical characters, but in the case of the monoclinic pyroxene, minute, measurable crystals were obtained. The sp. gr. of the different forms are as follows: glass (MgSiO_3), 2.743; orthorhombic amphibole, 2.857; monoclinic amphibole?, orthorhombic pyroxene, 3.175; and monoclinic pyroxene, 3.192.

The order of stability of these four polymorphic forms is the same as that of their specific gravities. Monoclinic pyroxene is stable at all temperatures, and the others are monotropic towards it; they change into it at an elevated temperature (orthorhombic pyroxene at 1250°) with development of heat.

Monoclinic pyroxene, the most stable of the four forms, was obtained in several different ways: (1) by crystallising a fused mass of the same composition; (2) by heating the glass (MgSiO_3 ; melting point 1521°) to a temperature above 1300° ; (3) by heating any of the other crystalline forms; (4) by the action of molten magnesium chloride or tellurite on amorphous silica; (5) by recrystallising magnesium silicate from a flux of magnesium chloride, magnesium vanadate, calcium vanadate, or tellurium dioxide. The minute crystals obtained by the last method have the same prism-angle, 88° , as ordinary diopside, but the other angles differ; the optical characters of this magnesian, monoclinic pyroxene are identical with those of the pyroxene of the Bishopville meteorite.

Orthorhombic pyroxene, enstatite, crystallises at lower temperatures than the monoclinic pyroxene, and was obtained by heating the glass between 1000° and 1100° . Large crystals were obtained in silicate (magmatic) solutions.

Monoclinic amphibole forms in very small quantities by rapidly cooling the fused mass, and also when the orthorhombic amphibole is heated with water at $375\text{--}475^\circ$.

Orthorhombic amphibole, kupfferite, is obtained by heating the molten silicate far above the melting point, at about 1600° , and then cooling rapidly in the air.

In many of the experiments, crystals of forsterite (Mg_2SiO_4) were obtained with the other products; optical and crystallographic determinations were made on this material.

L. J. S.

Composition of some Montreal Minerals. B. J. HARRINGTON (*Trans. Roy. Soc. Canada*, 1905, [ii], 11, (3), 25—28).—The following minerals are found in the Corporation Quarry, at the back of Mount Royal.

Nephelite-syenite is a pale flesh-red, translucent, vitreous to slightly greasy in lustre, and shows no marked cleavage, but sub-conchoidal to uneven fracture (anal. I.).

Amite (ægirite) occurs in deeply-striated prisms, mostly greenish-black or brown; has a subvitreous lustre, is nearly opaque, and has a hardness approaching 6, and a sp. gr. 3.521; it fuses quietly to a black, magnetic glass (anal. II.).

Lepidomelane occurs in rough, black crystals, which are green by transmitted light, and has a vitreous lustre and a small optic axial angle; it has the hardness 3, and a sp. gr. 3·269, is readily decomposed by hydrochloric acid, and when fused over the blowpipe forms a black, magnetic slag (anal. III.). If the titanium dioxide is calculated with the silica, this mineral has the composition $5(R_2O, RO), R_2O_3, 4SiO_2$.

Natrolite is white, translucent, and vitreous, has the hardness 5, and a sp. gr. 2·234, gelatinises readily when treated with hydrochloric acid, and fuses to a glass colouring the flame yellow (anal. IV.).

Analcite forms large, white, translucent trapezohedrons with vitreous lustre, and has a hardness slightly greater than 5 and a sp. gr. 2·22 (anal. V.).

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	Na ₂ O.	K ₂ O.	Li ₂ O.	H ₂ O.
I.	44·98	—	32·65	0·72	—	—	trace	—	16·08	4·54	—	0·97
II.	49·51	0·61	2·72	22·26	5·82	1·51	7·16	1·09	8·62	0·38	—	0·57
III.	32·96	2·80	10·34	8·85	27·19	2·79	0·64	0·73	0·98	7·75	0·03	4·36
IV.	47·09	—	26·99	trace	—	—	trace	—	16·46	0·01	—	9·80
V.	54·83	—	24·20	—	—	—	0·08	—	12·01	—	—	8·50

G. Y.

Metallic Iron found at Magdeburg in 1831. FRITZ RINNE (*Jahrb., Min.*, 1906, ii, 61—89).—The composition and micro-structure of this pseudo-meteorite point undoubtedly to an iron of artificial origin.

L. J. S.

Physiological Chemistry.

Carbon Monoxide in Normal Blood. RAPHAEL LÉPINE and BOULUD (*Compt. rend.*, 1906, 143, 374—375).—Carbon monoxide occurs in the blood of normal dogs (Nicloux) and in cases of anæmia. The view that oxalic acid is its source is supported by the fact that intravenous injection of sodium oxalate in dogs increases the amount present eight- or ten-fold. In asphyxia, however, the formation of the gas is prevented. Dextrose or lævulose similarly administered has a similar result; this is attributed to increased oxalic acid formation. Tartaric acid produces the same effect but less rapidly, whereas lactic acid does not. W. D. H.

Hydroxyl-ions of Fœtal (Placental) Blood. ALEXANDER SZILI (*Pflüger's Archiv*, 1906, 115, 72—81).—The placental blood has the same amount of titratable alkali as that of the mother. The two are in osmotic equilibrium. In both cases the smallest amount of hydroxyl-ions does not correspond with the lowest amount of titratable alkali. W. D. H.

Alcohol in Normal Blood and Tissues. W. HUTSON FORD (*J. Physiol.*, 1906, 34, 430—443).—A republication of results affirming

the existence of alcohol in the blood and tissues in small amounts. These were obtained originally in 1858. The facts are believed to be important in view of the calorific value of alcohol. W. D. H.

Glycerol of the Blood, and its Investigation by Zeisel's Iodide Method. FRANZ TANGL and STEPHAN WEISER (*Pflüger's Archiv*, 1906, 115, 152—174).—The blood contains free glycerol; glycerylphosphoric acid could not be found. Glycerol is present in the plasma, not in the corpuscles. Horses' blood contains 0.076, horses' plasma 0.095, and ox-blood 0.07 gram of glycerol per 1000 grams. W. D. H.

The Sugar of the Blood. RAPHAEL LÉPINE and BOULUD (*Compt. rend.*, 1906, 143, 500—504, 539—542).—The sugar of the blood is mainly in combination, and this "masked sugar" is liberated with comparative ease. The total sugar obtained from the blood is increased by the action of phloridzin, and by the enzymes emulsin and invertin, and also to nearly as great an extent by merely keeping the blood at 60°, a temperature sufficiently high to prevent glycolysis, but not high enough to inhibit the ferment which presumably disengages the sugar. The amount of increase in the sugar is not constant.

The sugar of normal serum does not dialyse, but when the masked sugar has been liberated it passes through. This favours the supposition that the sugar is not free in the blood, but that it is combined loosely with albuminous material. If this is so, the fact that it does pass readily into the urine is intelligible. W. D. H.

Amino-acids in Blood and Lymph. WILLIAM H. HOWELL (*Amer. J. Physiol.*, 1906, 17, 273—279).—By means of dialysis through collodion membranes, amino-acids may be separated from both blood and lymph by means of β -naphthalenesulphonic chloride. In the blood, a positive reaction is obtained even after fifty hours' abstinence from food, but much more of these substances are obtained in well-fed animals, especially in the portal blood. The membrane used is permeable to proteoses and peptone, but none was found. The portal blood (owing probably to a higher percentage of proteid) has a permanent greater osmotic pressure than that collected from other parts. W. D. H.

Non-coagulable Proteid in Blood. WILLIAM H. HOWELL (*Amer. J. Physiol.*, 1906, 17, 280—296).—After the principal proteids of blood have been removed by heating in feebly acid reaction (acetic acid) to 80—85°, a proteid (Chabrie's albumon) remains in solution; it is, however, precipitated partially by prolonged boiling if the reaction is made strongly acid. It is not a peptone or proteose; it contains iron and a considerable amount of lecithin, which can be completely removed by boiling with alcohol. If serum-albumin is isolated and dialysed, it is not coagulable by heat in the presence of sodium, potassium, or lithium salts, but it is in the presence of ammonium, barium, calcium, or magnesium salts. Globulins treated in the same way are heat-coagulable in the presence of both sets of salts,

Fractional precipitation with salts is an unsatisfactory method of obtaining pure products. After a proteid has been salted out by ammonium sulphate, it is more susceptible to precipitation by heat or by dialysis.

It is suggested that the term serum-globulin should be restricted to euglobulin. The proteid left in solution after dialysis shows the essential properties of an albumin modified by combination with lecithin or a lecithin-containing complex. W. D. H.

Composition of Body-fluids in Marine Animals. SILVESTRO BAGLIONI (*Beitr. chem. Physiol. Path.*, 1906, 9, 50—66).—The blood serum of the dog-fish shows great variations in its percentage of proteid; the amount of non-proteid nitrogen is almost as great; this is mainly due to urea, as others have pointed out. During hunger the proteid nitrogen falls. The urea concentration in the blood is about three times greater than in the urine. In other selachian fishes the same holds good, but the actual amount of urea in the blood is smaller. In the teleostean fishes, on the other hand, the conditions are similar to those in land animals. In the body fluids of various invertebrates, the amount of proteid is very variable, but is least in those lower forms which have not a closed vascular system; in higher molluscs and arthropods, the amount of proteid is important; the amount of extractive nitrogen per cent. is in the second or third decimal place; the amount in the urine is greater. Octopus' urine contains proteid; this may be an "alimentary albuminuria." The statements are all illustrated by tables of analyses. W. D. H.

Relative Concentration of Calcium Ions in reference to the Reversal of the Polar Effects of the Galvanic Current in Paramœcium. FRANK W. BANCROFT (*J. Physiol.*, 1906, 34, 444—463).—If *Paramœcia* are washed in distilled water and then subjected to weak solutions of many salts, they swim towards the anode, and the behaviour of the cilia indicates that the anode is the stimulating electrode. Complete absence of galvanotropism is best produced by salts which diminish the concentration of free calcium ions. The character of the galvanotropism depends on the relative amount of these ions which are present. W. D. H.

Relation of Ions to Contractile Processes. I. Action of Salt Solutions on Ciliated Epithelium. RALPH S. LILLIE (*Amer. J. Physiol.*, 1906, 17, 89—142).—The toxicity of numerous salts on cilia is described with full detail, and special attention is directed to antagonism or antitoxic action; this is in general due to an approximate equalisation of the opposite actions of anion and cation on the colloids of the tissue. Hence salts the toxicity of which is due to predominant anion action require salts with active cations to counteract them and *vice versa*. W. D. H.

The Rôle of Elementary Nitrogen in Animal Metabolism. CARL OPPENHEIMER (*Chem. Centr.*, 1906, ii, 809—810; from *Biochem. Zeit.*, 1, 177—182).—Experiments on healthy and diabetic dogs and also on

rabbits were made in order to ascertain whether atmospheric nitrogen plays any part in metabolism. The results were negative.

W. D. H.

Calcium and Magnesium Metabolism. S. GOITEIN (*Pflüger's Archiv*, 1906, 115, 118—151).—If the diet is rich in calcium and magnesium, the body enriches itself with these substances, whilst it loses them if the food contains but little. These changes mainly affect bone and muscle; the variations in other organs, especially as regards magnesium, are very small.

W. D. H.

Metabolism Experiments with Organic and Inorganic Phosphorus. J. A. LE CLERC and FRANK C. COOK (*J. Biol. Chem.*, 1906, 2, 203—216).—The nitrogen retained in rabbits and dogs is usually lowered (although the nitrogen balance is not necessarily negative) by the addition of inorganic phosphorus (phosphates) to the normal diet. If the food is poor in phosphorus, the addition of inorganic phosphorus lessens the digestibility of the nitrogen, and the nitrogen and phosphorus balances are generally negative. Organic phosphorus favours nitrogenous metabolism and increases the nitrogen and phosphorus retention. The phosphorus from wheat bran is specially valuable in this direction. The added phosphorus is never retained if the diet is normal. Organic phosphorus was never found in the urine.

W. D. H.

Digestibility and Utilisation of some Polysaccharides derived from Lichens and Marine Algæ. T. SAIKI (*J. Biol. Chem.*, 1906, 2, 251—265).—Experiments with lichenin from Iceland moss, Agar-agar, and preparations from kombu, wakame, and other Japanese fungi indicate that the polysaccharides present are not readily transformed into sugar by enzymes of animal or vegetable origin.

W. D. H.

Nitrogenous Metabolism as affected by Diet and by Alkaline Diuretics. H. D. HASKINS (*J. Biol. Chem.*, 1906, 2, 217—229).—In diets containing at least 5 grams of nitrogen daily, whether consisting of animal, vegetable, or mixed foods, the ammonia excreted varies with the total nitrogen, and the relative ammonia nitrogen to total nitrogen remains constant (not the absolute amount of ammonia as Folin states). The administration of sodium hydrogen carbonate and sodium citrate reduces the ammonia to one-third of the normal, and the urea increases correspondingly. In this case the fixed alkali given takes the place of ammonia in neutralising acids formed in the body, and this allows more ammonia to be converted into urea. The experiments were made on men.

W. D. H.

Action of Quinine on Ferments. ERNST LAQUEUR (*Chem. Centr.*, 1906, ii, 1074; from *Arch. exp. Path. Pharm.*, 55, 240—262).—On the supposition that the elective action of quinine on metabolism is due to elective action on enzymes, the following six ferments were selected for experiment: the autolytic ferment of the liver, pepsin, rennin, gastric lipase, and the catalase and oxydase of the blood. The tables given

show that quinine influences their actions to varying degrees, but the application of these results to metabolic processes is still for the future.

W. D. H.

Concentration of Hydrogen Ions in the Contents of the Fasting Human Stomach. FRANZ TANGL (*Pflüger's Archiv*, 1906, 115, 64—71).—The hydrogen ions in the contents of the fasting stomach arise from hydrochloric acid, that being the only acid present; the amount varied from 0.05 to 0.15 per cent.

W. D. H.

The Behaviour of Lecithin to the Lipolytic Ferments. C. SCHUMOFF-SIMANOWSKI and NADINE SIEBER (*Zeit. physiol. Chem.*, 1906, 49, 50—63).—Lecithin is decomposed by the steapsin of the gastric juice, but much more energetically by that of the pancreatic secretion. Lipases from plants act similarly. The lipase of the blood and blood-serum has no such effect.

W. D. H.

Influence of Bile on Pancreatic Ferments. OTTO VON FÜRTH and JULIUS SCHÜTZ (*Beitr. chem. Physiol. Path.*, 1906, 9, 28—49).—Bile favours the lipolytic action of pancreatic steapsin; a small quantity will raise the action fourteen-fold. Small changes in alkalinity have no effect, and bile ash has no such action. The action is due to the bile salts, especially to their cholic acid component; a few milligrams of a salt of this acid have a strong effect. Deoxycholic acid is nearly as active, but oxidation products of cholic acid (cholanic, bilianic, and cilianic acids) are inactive. A. W. Hewlett's statement that lecithin favours the action is confirmed, but the action of bile is not due to its lecithin. The degree of activation produced by bile and its salts is very variable, and so must be influenced by other factors. The favouring action of bile on trypsin is inconstant and its intensity much less than the similar action on the fat-splitting enzyme.

W. D. H.

The Cleavage of Food-proteid in the Intestine. OTTO COHNHEIM (*Zeit. physiol. Chem.*, 1906, 49, 64—71).—The combined action of pepsin and erepsin is sufficient to produce complete or almost complete cleavage of proteids. The experiments were made *in vitro*.

W. D. H.

Chemical Stimulation of Cerebrum. SAMUEL S. MAXWELL (*J. Biol. Chem.*, 1906, 2, 183—194).—A full account of experiments previously published (*Abstr.*, 1906, ii, 240).

W. D. H.

Nature of Electrical and Chemical Stimulation. WILLIAM SUTHERLAND (*Amer. J. Physiol.*, 1906, 17, 266—272). **A Molecular Theory of the Electric Properties of Nerve.** W. SUTHERLAND (*ibid.*, 297—311).—Speculative papers very much on the lines of A. P. Mathew's work.

W. D. H.

Influence of Osmotic Pressure on the Irritability of Skeletal Muscle. WALTER J. MEEK (*Amer. J. Physiol.*, 1906, 17, 8—14).—Hypertonicity depresses the contractility and excitability of skeletal muscle. Hypotonicity increases these properties. The action is on the muscular fibres themselves, because curare does not influence the above results. W. D. H.

Influence of Temperature on Striped Muscle and its Relation to Chemical Reaction Velocity. THEO. C. BURNETT (*J. Biol. Chem.*, 1906, 2, 195—201).—The processes underlying muscular contraction are chemical in nature. A rise of 10° in temperature doubles or trebles the velocity of a reaction. The length of the latent period was made the basis of calculation, and the formula would be latent period at tn : latent period at $tn + 10 = 2$ or 3. The results show that the figure is usually near 2, or between 2 and 3. W. D. H.

Extractives of Muscle. V. Carnitine. R. KRIMBERG (*Zeit. physiol. Chem.*, 1906, 49, 89—95. Compare this vol., ii, 781).—The substance in meat extracts described as carnitine is allied to the betaine-choline group. It contains trimethylamine. A nitrogenous acid was also separated as a barium salt, but the composition of this second component of the carnitine molecule is not yet decided. W. D. H.

The Relative Proportions of the Proteids of Muscle in Physiological and Pathological Conditions. PAUL SAXL (*Beitr. chem. Physiol. Path.*, 1906, 9, 1—27).—Investigations on the chemical composition of muscle made after *rigor mortis* has set in give an incorrect view of its proteid constituents. The three principal varieties of muscle (voluntary, cardiac, and smooth) differ in their proportion of soluble and insoluble proteids (muscle-plasma and muscle-stroma). The proportion in the three kinds of muscle is respectively 7 : 1, 1 : 3, and 1 : 4. The proportion between the soluble proteids paramyosinogen (von Fürth's myosin) and myosinogen (von Fürth's myogen) is 1 : 5. Muscular activity has no influence on such figures. In fatty degeneration of the heart, the total proteids are less, and in hypertrophy greater than normal. In phosphorus poisoning the soluble proteids of the heart increase, and the insoluble decrease. *Rigor mortis* is due to proteid coagulation, and the insoluble proteids therefore increase; the phenomenon is most marked in the voluntary muscles, for they contain so much soluble proteid to undergo coagulation; in heart muscle it is less marked, and in smooth muscle absent. In fatty hearts it is more marked than in normal cardiac tissue. The phenomenon is irreversible. W. D. H.

Sugar-yielding Substances in Liver. RUDOLF TÜRKEL (*Beitr. chem. Physiol. Path.*, 1906, 9, 89—90).—Seegen states that the total carbohydrate of the liver is greater than the sum of its sugar and glycogen, and that after both are removed a material remains which is precipitable by alcohol, and yields sugar by boiling with acids. In other organs he could not discover this substance. In the present research no sugar-yielding substance was found in the liver after the removal of proteid, glycogen, and the sugar already present. W. D. H.

Formation of Dextrorotatory Lactic Acid by the Autolysis of Animal Organs. JUNICHI MOCHIZUKI and R. ARIMA (*Zeit. physiol. Chem.*, 1906, 49, 108—112).—Magnus Levy states that in liver autolysis the lactic acid obtained is a mixture of the optically inactive with the dextrorotatory acid, in aseptic autolysis the latter comprises 40 per cent. of the whole, whilst in antiseptic autolysis it is only 10 per cent. The present research was carried out with bull's testes; during autolysis, the lactic acid increases; the zinc salt was identical with that of the dextrorotatory lactate. The nature of the material which gives rise to the acid, presumably by ferment activity, is unknown. Other organs are being examined. W. D. H.

Influence of Alkalinity on Liver Autolysis. ALEXIS VON DRJEWEZKI (*Chem. Centr.*, 1906, ii, 806; from *Biochem. Zeit.*, 1, 229—245).—If the concentration of alkali is 0.2 to 0.3 per cent., autolysis runs its usual course, except that proteid cleavage occurs more slowly. If the alkalinity is raised to 0.5 per cent. (in terms of sodium carbonate) autolysis ceases. In ordinary liver autolysis, proteoses are found abundantly. Among the mono-amino-acids glycine and leucine were identified; leucine comprises the main amount of this fraction.

W. D. H.

Proteolytic Action of Animal Tissue Juices, and of Intestinal Juice. EMIL ABDERHALDEN and YUTAKA TERUUCHI (*Zeit. physiol. Chem.*, 1906, 49, 1—14).—The authors have already shown that aqueous extracts of ox-liver contain active proteolytic ferments which split *dl*-leucylglycine and glycylglycine. The present paper is a continuation of the work with other organs and other peptides. As a rule, the expressed juice was used instead of, or as well as, aqueous extracts. Bacterial action was excluded by toluene. Ox-liver juice splits *dl*-leucyl-glycine and glycyl-*dl*-alanine, but not racemic leucyl-leucine nor glycine anhydride. Ox-muscle juice contains little or no proteolytic ferments, and so contrasts with rabbit's muscle; it decomposes glycylglycine, *dl*-leucylglycine and glycyl-*dl*-alanine, but only to a slight extent. Dog's muscle juice is more active. Dog's kidney juice is also active, but it and intestinal juice from the same animal do not decompose hippuric acid. Dog's liver juice is only active in the resolution of glycylglycine and glycyl-*l*-tyrosine. The intestinal juice secreted by the dog and ox is also very active in resolving the same peptides. Not only the organ, but the blood-serum of some animals is active in the same direction, although here possibly trypsin absorbed from the intestine has in part to be dealt with.

W. D. H.

The Behaviour of Leucylphenylalanine, Leucylglycylglycine, and Alanyl-glycylglycine toward the Liver-juice of the Ox. EMIL ABDERHALDEN and PETER RONA (*Zeit. physiol. Chem.*, 1906, 49, 31—40).—The three peptides mentioned are split to some extent by the juice expressed from ox-liver. The main object of these and similar experiments is to learn something of proteid cleavage and proteid-synthesis in the tissue-cells of the body. No reversible action

was ever observed ; various mixtures of amino-acids were never found altered by pancreatic juice, or various tissue juices. No synthesis of peptides occurred.

W. D. H.

Phosphorus and Calcium of Human Milk. ALFRED W. SIKES (*J. Physiol.*, 1906, 34, 464—480).—The average amount of phosphoric acid in human milk during the first fortnight after lactation starts is 0.029 per cent. The percentage of non-proteid phosphoric acid varies : in primipara (0.016) and multipara (0.018) ; the percentages of proteid phosphoric acid are 0.013 and 0.011 respectively. In primipara the total rises up to the ninth day ; in multipara the maximum is a little earlier. The variations are mainly due to the non-proteid phosphoric acid. The average amount of calcium for the same period is 0.03 per cent., and rather less in primipara. The greater part (84 per cent.) is combined with proteid. Variations from the average are small. The proportion of calcium to proteid is 1.06 : 100.

W. D. H.

Influence of Added Substances on the Rennin Coagulation of Cows' Milk. CHANA SMELIANSKY (*Arch. Hygiene*, 1906, 59, 187—215).—The longer milk is heated before the addition of rennin, the longer it takes to coagulate and the softer and in smaller pieces is the coagulate ; similarly, on dilution with water, the moment of coagulation is delayed, but the nature of the precipitate does not seem to be altered. On the addition of mucilage, prepared by heating starch with water and rubbing the pulp through a fine sieve, the time required for coagulation is if anything lessened, whilst the coagulate becomes softer and more loosely packed. Sodium carbonate delays coagulation and gives a softer coagulate ; sodium chloride has the same influence when at least 4 per cent. of the salt is added ; calcium salts have a similar action. A slightly alkaline milk coagulates more slowly and in finer flakes than a neutral or faintly acid milk. Milk sugar, dextrose, sucrose, or mannitol are without influence on the coagulation.

E. F. A.

Amino-acids in Normal Urine. JULIUS WOHLGEMUTH and CARL NEUBERG (*Chem. Centr.*, 1906, ii, 895 ; from *Med. Klin.*, 1906, No. 6).—From 8 litres of urine, 0.2 gram of glycine (as barium naphthyl-carbimideglycine ; compare Abstr., 1905, i, 647), or a percentage of 0.0025, was obtained. The quantity is not of physiological importance.

W. D. H.

Endogenous Purine Excretion in Man. JOHN J. R. MACLEOD and H. D. HASKINS (*J. Biol. Chem.*, 1906, 2, 231—242).—The excretion of endogenous purine substances is not affected by very great variations in diet, provided that this is purine-free. In different individuals the amount varies. Sodium citrate and sodium hydrogen carbonate, if given in amount sufficient to make the urine alkaline, increase the endogenous purine excretion ; this effect lasts for some days, even after the reaction of the urine again becomes acid.

W. D. H.

Detection of Toxic Bases in Urine. III. FRIEDRICH KÜTSCHER and ALBERT LOHMANN (*Zeit. physiol. Chem.*, 1906, 49, 81—87. Compare Abstr., 1906, ii, 786; FR. KÜTSCHER, *ibid.*, 88. Compare Abstr., 1906, ii, 471).—By fractional precipitation as platinum and gold salts, methyl- and dimethyl-guanidine were identified in the urine of normal people. Whether these are precursors or degradation products of creatinine will be discussed in a future paper.

The base described in the first paper of the series, which is toxic, was separated as a gold salt; it is di-acid, has the formula $C_{13}H_{26}N_4O_4$, and the name *kynosine* is proposed for it.
W. D. H.

Phosphorus Content of Fæces Fat. JOHN H. LONG and W. A. JOHNSON (*J. Amer. Chem. Soc.*, 1906, 28, 1499—1503. Compare this vol., ii, 637).—The amount of fat in eight samples of fæces varied from 8.60 to 19.45 per cent. (calculated on the dry material), whilst the phosphoric acid (P_2O_5) in the fat varied from 0.20 to 3.66 per cent. It is probable that the phosphorus is present in the form of "lecithans" or "phosphatides," substances in which the phosphorus and nitrogen ratios are variable. The probable sources of these phosphorus compounds in fæces fat are discussed.
E. G.

Ascitic Fluid containing Albumin Soluble in Acetic Acid. BRETET (*Ann. Chim. anal.*, 1906, 11, 368—370).—An ascitic fluid examined by the author contained 33.7 grams per litre of albumin which was readily soluble in acetic acid. Heating the fluid alone or with the addition of a little nitric acid produced an abundant coagulum, but the addition of acetic acid entirely prevented coagulation, even at a boiling temperature. The albumin present in the urine of the patient was coagulable in the presence of acetic acid.
W. P. S.

Hydrochloric Acid in Cancer. S. MONCKTON COPEMAN and H. WILSON HAKE (*Lancet*, 1906, ii, 1276—1277).—From the examination of the stomachs of 500 mice the conclusion is drawn that the hydrochloric acid is higher in those suffering from cancer than in normal mice. The analyses, however, were not made on the gastric contents only, as in the work of previous investigators, but on the contents *plus* the gastric tissue.
W. D. H.

Cancer. CARL NEUBERG (*Chem. Centr.*, 1906, ii, 902; from *Zeit. Krebsforschd.*, 2, 171. Compare Abstr., 1905, ii, 338).—A cancerous growth of the liver, secondary to one in the stomach, was examined, two-thirds of its nitrogen was present in the form of mono-, and one-third in di-amino-acids; bases, sulphur, phosphorus, and ash were also estimated, the net result being that the cleavage products are approximately in the same proportion as in normal cell-globulins. The statement of Blumenthal and Wolff that the fresh tumours resist peptic but not tryptic digestion was confirmed. The nucleo-proteid was prepared from an aqueous extract by precipitation with acetic acid, and an elementary analysis made; the percentage of phosphorus was 3.97. It gives intense phloroglucinol and orcinol reactions. On hydrolysis it yields orthophosphoric acid, pentose, and purine bases.

Autolysis in carcinomatous tissue increases under the action of Röntgen rays, and still more so under that of radium emanations.

W. D. H.

Hydroxyl-ion Concentration of Diabetic Blood. H. BENEDICT (*Pflüger's Archiv.*, 1906, 115, 106—117).—The concentration of hydroxyl ions in diabetic blood does not differ from that in normal blood, and even in diabetic coma, a depression of the concentration is not constantly present. The observations do not support the view that the coma is produced by acids.

W. D. H.

Effect of Castration on Metabolism in Osteomalacia. FRANCIS H. McCRUDDEN (*Amer. J. Physiol.*, 1906, 17, 210—217. Compare Abstr., 1905, ii, 845).—Castration is not a permanent cure. The present paper continues the history of the same patient. The course of metabolism later was different from what it was before the operation, but so little is known of inorganic metabolism that further experiments on normal people are contemplated. The disease is attributed by some to disease of the ovaries, but these are usually found to be normal on removal.

An incapacity of the ground substance of bone to fix inorganic salts, or an insufficient supply of such salts in the blood, do not seem to be the causes of the disease. There is, however, a specially active katabolism of the bony tissue, and this occurs even in ordinary pregnancy when the developing embryo requires a large supply of lime. An abnormal sulphur metabolism which occurs is secondary to this. Castration certainly prevents pregnancy, but it has no influence in the ultimate and at present unknown cause of the disease.

W. D. H.

Behaviour of Bromides in the Body. H. VON WYSS (*Chem. Centr.*, 1906, ii, 1077—1078; from *Arch. exp. Path. Pharm.*, 55, 263—287).—Administration of bromides leads to their appearance in the urine, and this goes on for a fortnight after the cessation of the administration. Large amounts are thus retained in the body for a considerable time. The brain, liver, and kidneys do not retain much; most was found in the blood serum. It is partly excreted in gastric and intestinal juices.

W. D. H.

Effect of Saline Purgatives. JOHN AUER (*Amer. J. Physiol.*, 1906, 17, 15—25).—Subcutaneous and intravenous injection of magnesium sulphate and chloride, sodium sulphate, phosphate and citrate, does not produce purgation in rabbits; they, however, do produce a moderate increase of peristalsis, except in the case of magnesium sulphate, which produces no effect at all.

W. D. H.

Biochemical Studies on Chloroform. JOHANN FEIGL and HUGO MEIER (*Chem. Centr.*, 1906, ii, 1135; from *Biochem. Zeit.*, 1906, 1, 317—331).—Perfectly pure chloroform has little or no effect on the blood pressure, the heart, or the vascular system; all the well-known effects are attributed to decomposition products of chloroform, especially carbonyl chloride. Biological tests are better than chemical

tests for determining whether a sample of chloroform is suitable for narcotic purposes. . P. H.

Action of Chloral Hydrate on the Heart. A. J. CARLSON (*Amer. J. Physiol.*, 1906, 17, 1—7).—Chloral hydrate has a primary stimulating action on the heart ganglion of *Limulus*, but if the drug is dissolved in plasma or sea-water surrounding the heart, the muscular tissue is depressed without primary stimulation. If the solution is applied to the entire heart, the tissues are paralysed in the following order: ganglion, nerves, or nerve-endings, muscle. These results are discussed in relation to similar experiments by Rohde and others in reference to the mechanism of cardiac excitability, but no clear statement of the author's views is made. W. D. H.

Importance of Thio-compounds in the Body. ALBERT EDINGER and PAUL CLEMENS (*Chem. Centr.*, 1906, ii, 1076—1077; from *Zeit. klin. Med.*, 59, 218—232).—The antiseptic action of quinoline bismuth thiocyanate is due to the setting free of hydrogen thiocyanate, and this action is supported by the presence of quinoline thiocyanate. Such compounds increase the excretion of sulphur and nitrogen, and lower the acidity of urine. Their toxic action is powerful and resembles that of hydrocyanic acid. By Rupp's method very small quantities of thiocyanate were found and estimated in various normal organs, even if none had been administered. W. D. H.

Physiological Action of some Bases obtained from Ox-muscle. FRIEDRICH KÜTSCHER and ALFRED LOHMANN (*Pflüger's Archiv*, 1906, 114, 553—568).—Particulars of lethal doses and physiological action on various animals are given in reference to novaine, oblitine, ignotine, and neosine. Oblitine acts harmfully on the intestine, and produces necrosis of the mucous membrane; it stimulates its muscular coat; it causes a lowering of arterial pressure and irregularity of the ventricle of the isolated frog's heart; it stimulates salivary secretion. After subcutaneous injection, none is found in the urine, but after it is given by the mouth, some passes as such through the body of the cat. Novaine has a very similar action, and some passes unchanged into the urine after subcutaneous administration. Probably both substances belong to the choline group. Only a very few experiments are recorded with ignotine and neosine; the former has a stimulating action and no effect on arterial pressure; the latter lowers arterial pressure slightly. W. D. H.

Subcutaneous Injection of Adrenaline. T. R. ELLIOTT and HERBERT E. DURHAM (*J. Physiol.*, 1906, 34, 490—498).—Subcutaneous injection of adrenaline in cats over prolonged periods did not, as some have stated, cause any production of anti-adrenaline. The muscles of the circulating system were unaffected. In one animal, the cervical sympathetic was unduly irritable, but it is doubtful if this was an effect of the drug. The suprarenal glands were somewhat enlarged; the liver and kidney underwent fatty degeneration. The same effects were noticed when the drug was given in milk by the mouth, so the

adrenaline, or some product of it which causes these changes, must be absorbed in the alimentary canal. The volume of the urine was unaltered, except during the immediate glycosuria which follows each injection.

W. D. H.

Action of Drugs on the Heart of Limulus. A. J. CARLSON (*Amer. J. Physiol.*, 1906, 17, 177—210. Compare this vol., ii, 558).—The action of alcohol, various anæsthetics, strychnine, caffeine, curare, nicotine, atropine, cocaine, pilocarpine, physostigmine, aconitine, veratrine, saponin, quinine, digitalin, adrenaline, and ergot were investigated. The action is the same as in the vertebrate heart, except in one or two instances where the statements of previous workers on the vertebrate heart are conflicting. Their primary action is on the local motor ganglion.

W. D. H.

Action of Ergot on the Alimentary Canal. SAMUEL J. MELTZER and JOHN AUER (*Amer. J. Physiol.*, 1906, 17, 143—166).—Ergot increases the natural movements of the stomach and intestines and augments the motor effect of the vagus. Its effect is antagonised to a great extent by atropine.

W. D. H.

Acid Intoxication. ALEXANDER SZILI (*Pflüger's Archiv*, 1906, 115, 82—105).—Two questions were investigated, namely, the alterations in the concentration of hydroxyl ions in the blood produced by intravenous injection of acid, and the depression in the same produced by lethal doses of acid. It was shown that the alkalinity of the blood does not sink in proportion to the amount of acid given, and that the cells only yield their alkali slowly to the blood to equalise the loss of alkalinity there. In fatal cases in rabbits the concentration of hydroxyl ions sinks by 95 per cent., and of titratable alkali by 78 per cent. In dogs the corresponding numbers are 96 and 75 respectively. The serum of all animals still reacted alkaline to lacmoid. In the experiments recorded, the dogs died more quickly than the rabbits, which is contrary to the generally accepted belief in the greater susceptibility of herbivora to acid poisoning. This point is discussed at length.

W. D. H.

Phosphorus Poisoning. EMIL ABDERHALDEN and ALFRED SCHITTENHELM (*Zeit. physiol. Chem.*, 1906, 49, 41—46).—In normal dogs, peptides given by the mouth or under the skin are broken down, and the nitrogen is discharged as urea. This is due to the presence of enzymes in the cells which act like trypsin. It was of interest to ascertain if the same happens when the animal is poisoned with phosphorus; *dl*-leucylglycine was given, but no altered dipeptide was found in the urine; small quantities of leucine and glycine were found, but it is uncertain if these came from the peptide administered; so in another experiment the liver juice of a dog poisoned by phosphorus was examined, but it cannot be stated with any certainty that its power of splitting peptides was less than that of normal liver juice.

W. D. H.

Can small amounts of Copper induce Chronic Poisoning?

MASATO TOYONAGA (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, 7, 25—28).—Two rabbits received daily 5 mg. of copper in a mixture of equivalent amounts of copper chloride and sodium carbonate. No copper could be detected in the fæces until, after five months, the daily amount was increased to 20 mg. The rabbits died soon afterwards, probably of cold. A small amount of copper was found in the liver, but none in the brain. There were no symptoms of poisoning.

Experiments were also made with manganese. A rabbit received 27 grams of manganese chloride in eleven months without any effect.

N. H. J. M.

Hydrocyanic Acid Poisoning. ANGELO DE DOMINICIS (*Chem.*

Centr., 1906, ii, 620—621; from *Boll. Chim. Farm.*, 45, 367—372. Compare Abstr., 1905, ii, 746).—The elimination of hydrocyanic acid occurs through the lungs. Some of the poison unites with the blood pigment to form cyanohæmoglobin.

W. D. H.

Lysol Poisoning. FERDINAND BLUMENTHAL (*Chem. Centr.*, 1906,

ii, 620; from *Biochem. Zeit.*, 1, 135—152).—The capacity of the organism to burn cresol is very great. By giving lysol to dogs in non-toxic doses, the cresol, ethereal sulphates, and glycuronic acid in the urine rise in amount proportional to the dose given. The destruction of cresol does not occur in the blood, but in the tissues, probably of the liver; the removal of its poisonous characters is largely due to union with sulphuric and glycuronic acids.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Vitality and Activity of Technical Lactic Acid Bacteria.

I. CARL WEHMER (*Chem. Zeit.*, 1906, 30, 1033—1034).—Lactic acid bacteria kept on dry, calcium lactate for six years were still able to set up lactic fermentation of sugar even though they had not formed any spores; after ten years the bacteria had completely lost their activity. Rough calculations showed that the bacteria were able to produce about ten times their own weight of lactic acid; the yield, which does not as a rule exceed 60 to 70 per cent., is considerably influenced by the purity of the culture, but it is not as yet possible to account for the wastage in sugar. P. H.

Fermentation of Milk. FERDINAND BLUMENTHAL and WOLFF (*Chem. Centr.*, 1906, ii, 900; from *Charité-Ann.*, 29, 12—18).—Milk which has been kept for years may contain 50 per cent. of the lactose originally present. In the spontaneous acid fermentation of milk

there is no essential peptonisation of proteids; large amounts of amino-acids, especially leucine, are formed. The only aromatic compound found is tryptophan. The amounts of acids are increased by prolonged putrefaction, the lactic acid more than succinic acid.

N. H. J. M.

Micro-organisms of Natto. SHIN SAWAMURA (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, 7, 107—110).—Natto is vegetable cheese prepared by fermenting boiled soy-beans. The micro-organisms consist at first chiefly of bacilli, but subsequently micrococci predominate.

Two bacilli were isolated, one of which produces the desired taste and aroma, but insufficient viscosity; whilst the second produces cheese of stronger viscosity, but less desirable as regards taste. It is probable that both bacilli are necessary for the production of perfect cheese.

Both bacilli produce diastatic enzymes.

N. H. J. M.

Action of Copper Salts on the Germination of Penicillium. LE RENARD (*Compt. rend.*, 1906, 143, 607—608).—Spores of *Penicillium crustaceum* are not killed (compare Benecke, Abstr., 1896, ii, 572), but rendered inactive by treatment with copper salts (acetate, chloride, nitrate, or sulphate), even in such dilute solutions as 0.00005 gram per litre, and can be stimulated to germination by subsequent treatment with solutions of potassium, ammonium or magnesium succinate or acetate of strengths comprised between decinormal and centinormal.

M. A. W.

The Separation of the Life and Ferment-action of Yeast. THOMAS BOKORNY (*Pflüger's Archiv*, 1906, 114, 535—544).—Sulphuric acid (0.05 per cent.) renders zymase inactive, and also kills yeast cells. The strength of the acid can, however, be adjusted so that the cells are killed, whereas the activity of zymase is hardly affected. Similar results were obtained with formaldehyde and mercuric chloride. They are stated quantitatively.

W. D. H.

Formation of Fusel Oil in Fermentation by Means of "Acetondauerhefe." HANS PRINGSHEIM (*Ber.*, 1906, 39, 3713—3715. Compare Abstr., 1905, ii, 848).—The author confirms the results of Buchner and Meisenheimer (this vol., ii, 790), who found that only very small quantities of fusel oil are produced when sucrose is fermented by expressed yeast juice. In the fermentation of sucrose by "Acetondauerhefe" no fusel oil was detected when the fermentation was conducted either in the presence or in the absence of leucine.

A. Mc. K.

New Variety of Mycoderma Yeast as a Cause of a Saké Disease. TEIZŌ TAKAHASHI (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, 7, 101—104. Compare Abstr., 1905, ii, 473).—A sample of turned saké (rice wine) yielded a new variety of yeast, *Mycoderma saprogenes saké*. The mycoderma grows on Mayer's and Nägeli's solution containing 9 per cent. of alcohol, whilst Hayduck's solution, with 2 and 4 per cent. of acetic acid, is unfavourable. It assimilates dextrose, levulose,

and sucrose, and also, to a less extent, maltose and galactose. It ferments dextrose and galactose very feebly, but not lævulose, sucrose, and maltose, and it does not assimilate nitrates and nitrites.

When cultivated in Hayduck's solution for seventeen days at 27—30°, a trace of volatile substance resembling altered vinegar in taste is produced. After five months' cultivation in saké with 13·85 per cent. of alcohol a trace of ethyl alcohol was found, but no aldehyde, methyl alcohol, or acetone.

The mycoderma is at once killed at a temperature of 70°, and in five minutes at 55°.

N. H. J. M.

Rôle of Enzymes in the Conversion of Organic Phosphorus Compounds in Germinating Seeds. W. ZALESKI (*Chem. Centr.*, 1906, ii, 893—894; from *Ber. deut. bot. Ges.*, 24, 285—291).—Experiments with seedlings of *Lupinus angustifolius* showed that the proteids containing phosphorus and phosphatides (chiefly lecithin) are decomposed by enzymes with production of inorganic phosphates. It is probable that the separation of phosphorus from proteids and proteolytic decomposition may take place independently of each other.

N. H. J. M.

Composition of Seed-Beet Shoots and of Beet Seedlings. OTTOKAR FALLADA (*Chem. Centr.*, 1906, ii, 904; from *Oesterr.-ung. Zeit. Zucker-Ind. Landw.*, 35, 269—273).—The dry matter (10·21 per cent.) of shoots of stored seed-beet contained: proteids, 14·76; nuclein, 8·31; nitrogenous compounds other than proteid, 16·56; crude fat, 1·05; nitrogen-free extractives, 47·18; crude fibre, 12·59; and ash 7·86 per cent. The ash contained $K_2O = 38·20$ and P_2O_5 , 16·36 per cent. Small amounts of copper-reducing compounds were found; sucrose, oxalic acid, and lecithin were not present.

The dry matter (11·37 per cent.) of seedlings contained: proteids, 24·11; non-proteid nitrogenous compounds, 7·62; fat, 7·45; non-nitrogenous extractives, 34·02; crude fibre, 15·11; and ash, 11·69 per cent.

N. H. J. M.

Mechanism of Carbon Assimilation in Green Plants; Photolytic Decomposition of Carbon Dioxide in Vitro. FRANCIS L. USHER and J. H. PRIESTLEY (*Proc. Roy. Soc.*, 1906, B., 78, 318—327. Compare this vol., ii, 299).—Phytolytic decomposition of aqueous carbon dioxide into formaldehyde and hydrogen peroxide, with production of formic acid as intermediate product, can take place in presence of chlorophyll when the necessary physical and chemical conditions are present, independently of vital or enzymic activity.

The process of photosynthesis can be reconstructed outside the green plant as far as the production of formaldehyde and oxygen by introducing a suitable enzyme; and as far as the production of oxygen and starch by introducing, in addition, certain kinds of non-chlorophyllous living protoplasm.

Formic acid is a product of the photolytic decomposition of carbon dioxide in presence of an inorganic uranium salt; formaldehyde is probably an intermediate product.

N. H. J. M.

Changes in the Nitrogenous Constituents of Green Plants in the Absence of Light. A. KIESEL (*Zeit. physiol. Chem.*, 1906, 49, 72—80).—By keeping a green plant (*Trifolium pratense*) in the dark, there is not only an increase in its asparagine, as had been previously stated, but also in other amino-acids, especially leucine, and also in the bases precipitable by phosphotungstic acid, among which arginine was identified; histidine is probably present also, but the amount obtained was too small to admit of a complete analysis. These bases cannot be obtained from healthy plants. W. D. H.

Direct Action of Light on the Transformation of Sugars absorbed by the Young Plants of *Pinus Pinea*. W. LUBIMENKO (*Compt. rend.*, 1906, 143, 516—519. Compare this vol., ii, 624).—Experiments were conducted on embryos of *Pinus Pinea* placed in sterilised solutions of sucrose, dextrose, maltose, lactose, galactose, or arabinose, and exposed to light of varying intensity, from full daylight to complete darkness. The young plants were weighed at the beginning and the end of the experiment, and it was found that whilst the light had no effect on the assimilation of maltose, lactose, lævulose, or galactose, the absorption of sucrose, dextrose, or arabinose varies greatly with the intensity of the light. In the original the results are represented in curve form, the percentage increase in weight as ordinates being plotted against the intensity of the light as abscissæ; the maximum increase in weight corresponds with an intensity of light too feeble for the assimilation of carbon dioxide by the chlorophyll, and as the intensity of the light increases, the amount of sugar absorbed by the plant diminishes, but at the same time the plant increases in weight owing to the decomposition of carbon dioxide by the chlorophyll. M. A. W.

Nature of the Cyanogenetic Glucoside in the Seeds of *Eryobotyra Japonica*. HENRI HÉRISSEY (*J. Pharm. Chim.*, 1906, [vi], 97, 350—355).—Fresh seeds of *Eryobotyra* contained 1—1.10 per cent. of amygdalin. No other glucoside acted on by emulsin was found. The leaves contain no cyanogenetic glucoside.

N. H. J. M.

Presence of Hydrocyanic Acid in Various Plants. ALEXANDRE HÉBERT (*Bull. Soc. chim.*, 1906, [iii], 35, 919—921. Compare Abstr., 1899. ii, 377; Pouchet, *Bull. Acad. Med.*, 1904, [iii], 52, 611; and Boman, *Bull. Mus. hist. nat.*, 1905, 337).—Three species of *Stipa* bearing the vernacular names Viscachera Azul-Pampa, Viscachera Pucara, and Viscachera Pusques (?Susques) have been examined, and the second of these was found to contain a cyanogenetic glucoside and an emulsin-like ferment, which interact in presence of water to yield hydrocyanic acid. No glucoside or enzyme could be detected in the first or third species. T. A. H.

Presence of Hydrogen Cyanide in the Distillates of some Belgian Plants. P. JITSCHY (*J. Pharm. Chim.*, 1906, [vi], 97, 355—358).—The same amounts of the different plants were macerated

with water and steam distilled. The following amounts of hydrogen cyanide obtained indicate roughly the relative amounts of glucoside present: *Ranunculus repens*, 0·00877; *Gynerium argenteum*, 0·02307; *Melica altissima*, 0·01543; *M. nutans*, 0·01821; *M. uniflora*, 0·00706; and *M. ciliata*, 0·01014.

N. H. J. M.

Fatty Oils from the Seeds of the Berries of *Rhamnus cathartica*. N. KRASOWSKI (*J. Russ. Phys. Chem. Soc.*, 1906, 38, i, 144—161).—The oil, when extracted from the crushed berries with ether, purified and dried, is greenish-brown, almost odourless, sparingly soluble in alcohol, readily so in ether, chloroform, or benzene; it dries slowly when exposed in thin layers, does not solidify at 20°, and has a sp. gr. 0·9195 at 15°/0°. It has the saponification number 186·0, iodine number 155·1, and acid number for the free acids 5·64. The non-volatile acids have the iodine number 160·63, the mean molecular weight 288·9, and the acetyl number 25·8. The mean molecular weight of the solid acids is 280·08, and the iodine number of the liquid acids is 172·4. The oil contains (1) 0·48 per cent. of phytosterol, the acetyl compound of which melts at 117—118° (Hesse 120°); (2) 0·11 per cent. of bright, leaf-like crystals melting at 81—82°, probably a saturated hydrocarbon of high molecular weight; (3) 0·24 per cent. of volatile acids, chiefly butyric acids, and a small quantity of a solid acid; (4) non-volatile acids, consisting of stearic acid 6, palmitic acid 1·12, oleic acid 30·10, linoleic acid 35·20, and linolenic and *iso*-linolenic acids 22·40 per cent.; (5) glycerol 4·3 per cent. The oil also contains certain colouring principles.

Z. K.

Formation and Physiological Rôle of Pentosans in Plants.

GIUSEPPE A. CALABRIN (*Chem. Centr.*, 1906, ii, 964; from *Staz. sper. agrar. ital.*, 39, 69—96).—Pentosans seem to be formed in young plants, the amount decreasing later on. In different cereals, the more resistant ones seem to contain more pentosans than the others. The roots of sugar beet generally contain less sucrose when the amount of pentosans is high. The amount of pentosans in plants is always greater when nutritive constituents are low.

N. H. J. M.

Researches on the Carbohydrates occurring in Spices. I.

Canella Bark. JOSEF HANUS and FRANZ BIEN (*Zeit. Nahr. Genussm.*, 1906, 12, 395—407).—The quantity of pentosan contained in spices is fairly constant for one and the same kind, the largest amount being found in the bark of *Canella alba*; next in order of pentosan content follow those spices which consist of the whole plant or leaves; then come barks, fruits, and seeds, and, lastly, flowers. The quantity of crude fibre yielded by a spice is generally proportional to the amount of pentosan present. Canella bark contains about 8 per cent. of mannitol, together with small quantities of araban and galactan and traces of xylan. The residue obtained after extracting canella bark with water still contains polysaccharides which dissolve on treatment with 5 per cent. sulphuric acid, and are apparently xylan and dextrosan. The pentosans occurring in canella bark are not hydrolysed completely by 8 per cent. sulphuric acid; a considerable proportion, closely allied to cellulose, remained unattacked.

W. P. S.

Hemicelluloses. NICOLA CASTORO (*Zeit. physiol. Chem.*, 1906, **49**, 96—107. Compare Shulze and Castoro, *Abstr.*, 1903, i, 152, 793).—The hemicelluloses from the seeds of *Ruscus aculeatus* yield mannose and a small amount of arabinose on hydrolysis. They thus contain a mannan and an araban; these serve as reserve material, and during germination are decomposed. The husks of the same seeds yield galactose, and the husks of the seeds of *Lupinus angustifolius* and of *L. albus* yield galactose and arabinose, and those of *Pinus Cembra* galactose and xylose. J. J. S.

Origin of Alkaloids in Plants. AMÉ PICTET (*Arch. Pharm.*, 1906, **244**, 389—396).—See *Abstr.*, 1905, i, 541. C. F. B.

Formation of Anthocyanin in Barley Stems. SHIGEHIO SUZUKI (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, **7**, 29—37).—The results of pot experiments indicated that the reddening of straw is due to deficiency of phosphoric acid or nitrogen, or of both.

N. H. J. M.

An Instance of the Formation of Anthocyanin under the Influence of the Bite of an Insect (*Eurhipara urticata*). MARCEL MIRANDE (*Compt. rend.*, 1906, **143**, 413—416).—The caterpillar *Eurhipara urticata* forms a hiding place in the folded leaf of *Galeopsis Tetrahit*, and having previously injured by means of a bite the under side of the leaf stalk, induces the premature formation of the violet-red, autumn colouring anthocyanin.

The formation of anthocyanin in leaves by means of natural or artificial injuries has frequently been observed, but the chemical nature, the cause of formation and the biological rôle of this colouring matter are at present unknown. M. A. W.

The Ultimate Red Coloration of certain Leaves, and the Colour of Autumn Leaves. ARMAND GAUTIER (*Compt. rend.*, 1906, **143**, 490—491).—A claim for *priority* against Mirande (preceding abstract. Compare *Abstr.*, 1892, 1242). M. A. W.

Fresh-water Algæ as Human Food. S. NAMIKAWA (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, **7**, 123—124).—Two edible algæ are found in Japan: *Nostoc Phylloderma* and *Prasiola Japonica*. The dry matter of *Nostoc* contains per cent.:

Crude proteid.	Crude fat.	Crude fibre.	Pentosans.	Galactan.	Starch, &c.	Ash.
24.75	0.93	3.64	4.56	1.86	58.40	12.28

The dried product when extracted with cold water yields a liquid pinkish-red by transmitted light, and reddish-violet by reflected light. Mineral acids and acetic acid change the colour to violet, whilst alkalis decolorise it. N. H. J. M.

Carbohydrates of Cocoa. A. D. MAURENBRECHER and BERNHARD TOLLENS (*Ber.*, 1906, **39**, 3576—3581. Compare Dekker, *Abstr.*, 1903, ii, 172).—Cocoa kernels contain 2.25 per cent. of pentosans before, or

5.51 per cent. after, extraction of the fat. The aqueous and alcoholic extracts of the powdered cocoa reduce Fehling's solution only slightly; the alcoholic extract is slightly lævorotatory. The product of the hydrolysis of the powder with 4 per cent. sulphuric acid contains theobromine, *l*-arabinose, *d*-galactose, and dextrose. The shells of the cocoa-beans contain 9.02—9.09 per cent. of pentosans; *l*-arabinose, *d*-galactose, dextrose, and perhaps xylose are present in the product of the hydrolysis. *l*-Arabinose and *d*-galactose are obtained also on hydrolysis of the fruit after removal of the seeds. Arabin and galactan must be present in the fruit, in the shells of the seeds, and in the kernels.

On repeated extraction of cacao butter with alcohol, a substance is obtained which melts at 133—137° (phytosterol) and has $[\alpha]_D - 33.5^\circ$, but gives the reactions of cholesterol. G. Y.

Examination of Eriodictyon. FREDERICK B. POWER and FRANK TUTIN (*Pharm. Rev.*, 1906, 24, 300—304).—This is an historical review and a summary of the results of the authors' investigations into the composition of Eriodictyon, the dried leaves of *Eriodictyon californicum* (U.S. Pharmacopœia, 1905). The essential oil, which amounts to 0.1 per cent. of the leaves, is a yellow liquid, has the characteristic odour of eriodictyon, a sp. gr. 0.9372 at 15°/15°, and $[\alpha]_D - 0^\circ 24'$, and is readily soluble in 70 per cent. alcohol. The leaves contain about 29.2 per cent. of their weight of resins, 75 per cent. of which are soluble in ether. The following substances have been isolated; the percentages given are the approximate amounts present in the leaves: triacontane melting at 65.2° and pentatriacontane melting at 74.5—75° (0.7 per cent.); formic, acetic, cerotic, and other acids in the free state, and glycerides of formic, butyric, and other acids, the total acids free and combined amounting to 0.5 per cent.; a very small amount of a *phytosterol* melting at 136—137°; *eriodictyol*, $C_{15}H_{12}O_6$, which is crystalline, melts at 267°, and has the properties of a phenol (0.23 per cent.); *homoeriodictyol*, $C_{16}H_{14}O_6$, which is crystalline, melts at 223°, and is of phenolic nature (3 per cent.); a yellow, crystalline, phenolic substance, $C_{16}H_{41}O_6$ ($C_{16}H_{14}O_6$?) (0.014 per cent.), and considerable amounts of dextrose.

The peculiar odour observed by Thal on heating the leaves with dilute sulphuric acid is that of furfuraldehyde. Quirini's eriodictyonic acid was an impure substance and probably consisted largely of homoeriodictyol. G. Y.

Examination of Grindelia. FREDERICK B. POWER and FRANK TUTIN [*Proc. Amer. Pharm. Assoc.*, 1905 (*Reprint*)].—The chief constituents of Grindelia (B.P.), from *Grindelia robusta*, are amorphous resins amounting to 21.6 per cent. of the whole. The portion soluble in light petroleum contains hentriacontane melting at 68°, a crystalline substance melting at 166°, which is either an isomeride or a lower homologue of phytosterol, formic acid together with traces of higher fatty acids, and a dark-coloured, amorphous product, which on fusion with potassium hydroxide yields chiefly formic and acetic acids. The ethereal extract of the resins, when fused with potassium hydroxide,

yields formic, acetic, and higher acids of the fatty series, together with the molecular compound of protocatechuic and *p*-hydroxybenzoic acids melting at 194° (Abstr., 1904, ii, 763).

Grindelia contains further a considerable amount of a laevorotatory sugar, probably *l*-glucose, proteid substances, an amorphous colouring matter, and tannin. Only traces of an essential oil having the characteristic odour of *grindelia* are obtained. The presence of a saponin or of an alkaloid as observed by previous authors cannot be confirmed.

G. Y.

Olive Leaves. FRANCESCO CANZONERI (*Gazzetta*, 1906, 36, ii, 372—376).—In this preliminary note the author describes briefly the compounds extracted from olive leaves by 95 per cent. alcohol. These are: (1) A faintly acid, non-nitrogenous compound, $C_{25}H_{44}O_3$ or $C_{24}H_{42}O_3$, which crystallises in tufts or fan-shaped aggregates of white, silky, prismatic needles, and melts and decomposes and partly sublimates at 297—298°; it emits an odour of incense when burnt on platinum foil, and dissolves moderately readily in ether or alcohol and sparingly in benzene. (2) A distinctly acid substance, which separates from alcohol in white, mammillary masses or a sticky powder melting at 253—255°; it dissolves readily in benzene or chloroform and sparingly in ether or carbon disulphide, and is possibly identical with the compound melting at 250° described by Peano (Abstr., 1903, ii, 173). (3) A substance crystallising in tetrahedra with curved angles and melting at about 236°. (4) A small quantity of an acid which crystallises in microscopic spherules (? octahedra), melts at 165°, and dissolves readily in alcohol or solutions of alkalis. (5) A compound which, when crystallised from acetic acid, melts at 180°; when treated with alkali, it becomes less soluble, and yields, on recrystallising from alcohol, portions melting between 200° and 236°. (6) Mannitol. (7) Tannic and gallic acids.

T. H. P.

Composition of the Fibrous part of the Japanese Orange. RANA BAHADUR (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, 7, 121—122).—The composition of the insoluble inside portions of Japanese oranges is as follows: hygroscopic water, 12·16; proteid, 5·27; ether extract, 1·28; galactan, 18·91; pentosan, 27·72; cellulose, 32·51; and ash, 2·15 per cent.

N. H. J. M.

Tea. A. D. MAURENBRECHER and BERNHARD TOLLENS (*Ber.*, 1906, 39, 3581—3582).—Dried Java tea from *Thea assamica* contains 5·60 per cent. of pentosans, caffeine, dextrose, traces of laevulose, or sucrose, araban, and galactan. Arabinose and *d*-galactose are obtained from the product of the hydrolysis with 6 per cent. sulphuric acid.

G. Y.

Organic Combination of the Phosphorus in Wine. ANGIOLO FUNARO and A. RASTELLI (*Chem. Centr.*, 1906, ii, 900—901; from *Staz. sper. agrar. ital.*, 39, 35—56).—Vines always contain lecithin from the period of grape formation, but the lecithin is partly decomposed during fermentation, whilst all that escapes decomposition

remains undissolved except in minute quantity. The phosphorus in wine is present chiefly as a phosphoglycerate produced from lecithin.

N. H. J. M.

Importance of Formaldehyde in Protecting Plants. G. KÖCK (*Chem. Centr.*, 1906, ii, 1012; from *Zeit. landw. Versuchs-Wes. Oesterr.*, 9, 811—843).—Formaldehyde is of value for protecting cereals and other cultivated plants from disease and for disinfecting green-houses; it is of little use when used for spraying vegetable parasites, and of hardly any use in the case of animal parasites.

N. H. J. M.

Injurious Action of Acetates and Formates on Plants. KEIJIRŌ ASŌ (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, 7, 13—24).—Solutions of alkali and calcium acetates and formates (0·5 per cent.) act injuriously on phænogams, but not on higher algæ, such as *Spirogyra*. The injury is probably due to the hydrolytic dissociation of the salts and the absorption of the base by proteids, leaving the acid in the free state.

N. H. J. M.

Proteids of Wheat. II. THOMAS B. OSBORNE and ISAAC F. HARRIS (*Amer. J. Physiol.*, 1906, 17, 223—230). III. T. B. OSBORNE and S. H. CLAPP (*ibid.*, 231—265. Compare Abstr., 1905, ii, 194).—The first paper relates to the methods of preparation and elementary analysis of the different proteids (leucosin, globulin, proteoses, gliadin, and glutenin). The following table gives the percentage composition:

	C.	H.	N.	S.	O.
Leucosin.....	53·03	6·84	16·80	1·28	22·06
Gliadin	52·72	6·86	17·66	1·14	21·62
Glutenin.....	52·34	6·83	17·49	1·08	22·26

The second paper deals with the cleavage products, and the following table gives the main results in percentages:

	Gliadin.	Glutenin.	Leucosin.
Glycine.....	0·0	0·89	0·94
Alanine.....	2·0	4·66	4·45
Aminovaleric acid	0·21	0·24	0·18
Leucine.....	5·61	5·95	11·34
α -Proline.....	7·06	4·23	3·18
Phenylalanine	2·35	1·97	3·83
Aspartic acid	0·58	0·91	3·35
Glutamic Acid.....	37·33	23·42	6·73
Serine	0·13	0·74	0·0
Tyrosine.....	1·20	4·25	3·34
Cystine.....	0·45	0·02	0·0
Lysine.....	0·0	1·92	2·75
Histidine	0·61	1·76	2·83
Arginine	3·16	4·72	5·94
Ammonia.....	5·11	4·01	1·41

Oxyproline was absent and tryptophan present in all cases.

W. D. H.

Stimulating Action of Calcium Fluoride on Phænogams. KEIJIRŌ ASŌ (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, 7, 85—89. Compare Abstr., 1903, ii, 173).—The results of water and soil culture experiments indicated that precipitated calcium fluoride probably had some stimulating effect. In water cultures of barley, calcium fluoride exerted a moderate stimulating action. It is suggested that the more favourable results obtained with Wiborg phosphate as compared with superphosphate may be due to the presence of 1 per cent. of fluorine in the former. As regards Ampola's results (Abstr., 1904, ii, 767) it is pointed out that the beneficial effect of calcium fluoride cannot be due to liberation of hydrogen fluoride, as carbon dioxide and weak acids have no action on it.

N. H. J. M.

[Influence of Manganese and Iron Sulphates and of Potassium and Sodium Silicates on Wheat and Barley]. JOHN A. VOELCKER (*J. Roy. Agric. Soc. Engl.*, 1905, 66, 206—211).—In the case of wheat, soaking the seed in solutions of manganese and iron sulphates (not more than 2 per cent.) is beneficial to germination. Barley is also benefited by manganese sulphate, and even 5 per cent. solutions are not injurious, whilst iron sulphate has no effect on germination. The yield of wheat is increased by soaking the seed in solution of iron sulphate, but not by manganese sulphate. Both salts when applied to the growing plant increase the yield of wheat and barley.

Potassium and sodium silicates are beneficial to wheat and barley, especially as regards the yield of straw.

N. H. J. M.

Degree of Stimulating Action of Manganese and Iron Salts on Barley. TOMIO KATAYAMA (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, 7, 91—93).—Whilst manganese sulphate (0.015 per cent.) gave with peas an increase of 50 per cent. of straw and 25 per cent. of seed, the increase in the case of cereals was only about 10 per cent. Recent pot experiments with barley showed that 0.01 per cent. of manganese and iron sulphates produced moderately increased yields of straw and grain (6.2 and 7.2 respectively), whilst the application of larger amounts resulted in decreased yields.

N. H. J. M.

Stimulating Action of Manganese on Rice. MUNESHIGI NAGAOKA (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, 7, 77—81. Compare *ibid.*, 6, 135).—Experiments on rice were repeated in 1904, under exceptionally favourable conditions of weather. The amounts of manganese sulphate applied varied from 30 to 170 kilos. per hectare, and the greatest gain due to manganese was 15 per cent. with 77 and with 107 kilos. per hectare.

The experiments were continued in 1905 on the same soil, now partially exhausted as regards minerals. Equivalent amounts of manganese sulphate, chloride, and carbonate (corresponding with $\text{Mn}_2\text{O}_3 = 25$ kilos. per hectare) were compared. The carbonate produced a slightly increased yield of straw, whilst with the sulphate and chloride the yield was reduced partly owing to acidity of the soil.

N. H. J. M.

Stimulating Influence of Sodium Fluoride on Garden Plants.

KEIJIRŌ ASŌ (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, 7, 83—84).—Pot experiments with *Helichrysum bracteatum* and *Pedicularia viscaria* showed that 0.02 gram of sodium fluoride in 8 kilos. of soil increased the yield of *Pedicularia*, but had very little effect on *Helichrysum*. With 0.2 gram of fluoride the result was almost the same as without fluoride.

N. H. J. M.

Condensed Vegetable Milk.

TOMIO KATAYAMA (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, 7, 113—115).—The condensed milk is prepared by concentrating soy-bean milk (Inouye, *Abstr.*, 1896, ii, 65) in a vacuum after adding sucrose (150 grams) and dipotassium phosphate (1 gram per litre). The product has a considerable nutritive value and can be used for preparing various foods.

The presence of vegetable milk in ordinary condensed milk can be detected by adding sodium carbonate, which produces a yellow coloration. Another means of detection is to add water (2 vols.) and a few drops of dilute sulphuric acid; when distilled, the characteristic odour of raw beans becomes noticeable.

N. H. J. M.

Vegetable Cheese from the Proteid of the Soy Bean.

TOMIO KATAYAMA (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, 7, 117—119).—Vegetable cheese was prepared by mixing pressed tofu (*Abstr.*, 1896, ii, 65), sodium chloride, lactose, and Swiss cheese (for the introduction of microbes). In one experiment some casein was also added. The mixture is kept moist for five months at 15°.

The product is grey, and is free from holes even when a considerable amount of lactose is employed. The taste differs from that of Swiss cheese.

N. H. J. M.

Composition of Soils from French Guinea.

ALEXANDRE HÉBERT (*Bull. Soc. chim.*, 1906, [iii], 35, 1033—1038).—Sixty-three virgin and cultivated soils and subsoils collected by M. Chevalier in various districts in French Guinea have been examined physically and chemically, and the results, which are tabulated in detail in the original, show that both the soils and subsoils are usually fairly rich in nitrogen and poor in phosphoric acid, potash, and lime.

T. A. H.

Agricultural Values of the Cacao Soils of S. Thomé and the Gold Coast Colony.

ALEXANDRE HÉBERT (*Bull. Soc. chim.*, 1906, [iii], 35, 1039—1041).—Five samples of soil from cacao plantations in S. Thomé, and three from plantations at Aburi, in the Gold Coast Colony, have been examined physically and chemically, and the results, which are tabulated in detail in the original, show that all the soils are deficient in lime and potash although comparatively rich in nitrogen and phosphoric acid. The deficiency in lime and potash is, however, less marked than in the case of the soils from French Guinea (see preceding abstract). The composition of vegetable *débris*, obtained from a plantation at Aburi, is also given.

T. A. H.

Formation of Humus.

SHIGEHIRA SUZUKI (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, 7, 95—99).—The amount of carbon dioxide liberated

from moistened leaves of *Quercus serrata*, both alone and with addition of calcium and magnesium carbonates and dipotassium phosphate, was determined every few days for about nine months.

The results showed that magnesium carbonate promotes the liberation of carbon dioxide, and that dipotassium phosphate has a very essential influence on the increase of carbon dioxide. Calcium carbonate had the opposite effect.

Leaves (with magnesium carbonate and dipotassium phosphate) which were first sterilised and then received the mycelium of a kind of *Penicillium*, liberated only about a third as much carbon dioxide as in the control experiment.

N. H. J. M.

Influence of the Reaction of the Manure on the Yield. KEIJIRŌ ASŌ and RANA BAHADUR (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, 7, 41—46).—Pot experiments were made with peas and barley manured with disodium phosphate, and with monosodium phosphate in conjunction with sodium nitrate and ammonium sulphate respectively. The results showed that the combination of acid manures or of alkaline manures is unfavourable, the best results being obtained with mixtures of acid and alkaline salts.

In the case of rice, sodium nitrate is unfavourable; ammonium sulphate with disodium phosphate gave the best result.

In experiments with onions, ammonium sulphate gave far better results than sodium nitrate when applied in conjunction with disodium phosphate and potassium carbonate.

The statement of Kruger and others that nitrification is unnecessary, ammonia under suitable conditions being as efficacious as nitrate, is confirmed.

N. H. J. M.

Application of Sodium Nitrate as Top-dressing for some Japanese Crops. KEIJIRŌ ASŌ (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, 7, 75—76).—Upland rice, *Sesamum* and *Colocasia antiquorum*, were manured with dung and superphosphate and with the same manures in conjunction with sodium nitrate as top-dressing. The nitrate increased the yield of *Colocasia*, but was almost without effect on rice and *Sesamum*.

N. H. J. M.

Manurial Value of Calcium Cyanamide. KEIJIRŌ ASŌ (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, 7, 47—52).—Experiments are described in which the effect of calcium cyanamide was compared with ammonium sulphate and with sodium nitrate. In the first series, buckwheat, *Sesamum*, and hemp were grown in soil unmanured for six years, in large zinc cylinders sunk into the ground. Further experiments in pots were made with upland and paddy rice, and hemp, which were grown in alluvial sand and diluvial loam containing 1 and 10 per cent. of humus respectively.

The results indicated that the manure is not inferior to ammonium sulphate and sodium nitrate. The only unsatisfactory result was that obtained with the paddy soil rich in humus.

N. H. J. M.

Efficacy of Calcium Cyanamide under Different Conditions.

R. INAMURA (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, 7, 53—55).—Calcium cyanamide acts more favourably in conjunction with superphosphate than with disodium phosphate when applied to *Brassica chinensis*.
N. H. J. M.

A Compound of Cyanamide as a Nitrogenous Fertiliser.

FRANK T. SHUTT and H. W. CHARLTON (*Trans. Roy. Soc. Canada*, 1905, [ii], 11, (3), 73—78. Compare Seelhorst and Müther, this vol., ii, 47; Bartsch, *ibid.*, 481; Feilitzen, *ibid.*, 487; Wein, *ibid.*).—Calcium cyanamidocarbonate is formed by passing a current of carbon dioxide through a solution of calcium cyanamide.

The growth of seedlings of wheat and peas is not affected by the presence of 5 mg. of calcium or potassium cyanamidocarbonate per 100 grams of soil; but as the amounts of these salts are increased, a toxic effect becomes apparent, and with 20 or more mg. of the salts per 100 grams of soil, the seedlings are rapidly destroyed.

The rate of nitrification of the cyanamide compounds in the soil is shown to decrease as the amounts of these are increased, indicating a toxic action on the nitrifying organisms.
G. Y.

Manurial Value of Different Potassium Compounds for Barley and Rice. KEIJIRŌ ASŌ (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, 7, 67—72).—In the case of barley, potassium chloride accelerated flowering and increased grain production. With rice, the yield was reduced. Potassium silicate gave the best results in several cases, and martellin is a favourable potassium manure for graminaceous crops. Potassium sulphate is favourable to straw production, whilst the carbonate was always less satisfactory when applied in conjunction with disodium phosphate.
N. H. J. M.

Effect of Various Potassium Manures on the Growth of *Colocasia antiquorum*. S. NAMIKAWA (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, 7, 73—74).—The bulbs of *Colocasia antiquorum* (sugar-potato) are rich in starch and are extensively used as food. On a loamy soil (limed), kainite and 30 per cent. potassium salts gave equally good results, somewhat better than wood-ash, which is the principal potassium manure in Japan.
N. H. J. M.

Relation of Sodium to Potassium in Soil and Solution Cultures. JAMES F. BREAZEALE (*J. Amer. Chem. Soc.*, 1906, 28, 1013—1025).—The plan of the experiments was to grow wheat plants for some days or weeks in a solution containing all the necessary food constituents and in similar solutions omitting sodium, potassium, both sodium and potassium, calcium and phosphoric acid respectively. All the plants were then removed to solutions containing full nutrient, and the amount of each constituent taken up from these solutions determined by analysing the solutions at the end of the experiment. The results showed that absence of any constituent in the solutions employed at the commencement resulted in an increased assimilation of the same constituent from the complete solution in which the plants

were afterwards grown. It was also found that the demand for potassium was greater when sodium was left out in the first period than when sodium was present all the time.

Further experiments are described in which radishes and beet were grown first in soils which had received sodium and potassium salts respectively, and then, for three to six days, in solutions containing full nutrient. The results obtained by analysing the solutions were similar to those in the previous experiments, and showed a greater demand for potassium in the plants grown in soil which had received no potassium for some years and a diminished demand where sodium had been applied.

N. H. J. M.

Lime Factor for Flax and Spinach. S. NAMIKAWA (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, 7, 57—60).—Flax was grown in soil containing $\text{CaO} = 0.458$ and $\text{MgO} = 0.374$ per cent., to which different amounts of calcium carbonate and magnesite were added so as to give the ratios $\text{CaO}:\text{MgO} = 1:1$, $2:1$, and $3:1$. In the case of spinach, sand was employed with addition of the two carbonates, the ratios being $1:2$, $1:1$, $2:1$, and $3:1$.

In both experiments the most favourable relation of calcium to magnesium was found to be $1:1$.

N. H. J. M.

Direct Manuring of Cereals with Different Forms of Calcium. A. LAZZARI (*Chem. Centr.*, 1906, ii, 903—904; from *Staz. sper. agrar. ital.*, 39, 5—17).—Calcium hydroxide gave better results than calcium carbonate.

N. H. J. M.

Regeneration of Over-limed Soil. S. MAKI and S. TANAKA (*Bull. Coll. Agr. Tōkyō Imp. Univ.*, 1906, 7, 61—65).—Nakamura (this vol., ii, 382) stated that a soil containing sufficient magnesium for crops, but a great excess of calcium in addition, is much benefited by manuring with magnesia so as to obtain a suitable ratio of $\text{CaO}:\text{MgO}$. The yield of barley was increased by 60 per cent.

Experiments with barley grown in sandy and loamy soils showed that over-liming may be remedied by adding magnesium sulphate, and that 14 parts of the crystallised sulphate are agronomically equivalent to 100 of magnesite.

N. H. J. M.

Analytical Chemistry.

Measurement of Standard and Other Solutions by Means of Chemical Measures. W. SCHLOESSER and C. GRIMM (*Chem. Zeit.*, 1906, 30, 1071—1073).—The authors have studied the question as to whether pipettes graduated by means of water always deliver the same volume of liquid, regardless of the nature of the liquid. The results obtained admit of no generalisations. The original paper should therefore be consulted for details. P. H.

Acidimetry by Measurement of Hydrogen. H. REBENSTORFF (*Chem. Centr.*, 1906, ii, 908; from *Zeit. phys.-chem. Unterr.*, 19, 201—213).—Magnesium turnings are recommended for displacing hydrogen from acids, the strength of which is to be determined by measurement of the volume of the displaceable hydrogen. P. H.

Preparation of Sulphuric Acid of Known Strength by Specific Gravity Determinations. A. H. W. ATEN (*Chem. Centr.*, 1906, ii, 1139; from *Chem. Weekblad*, 1906, 3, 523—526).—The author has devised an easy method for preparing sulphuric acid of any desired strength in large quantity. For this purpose he prepares a stock solution *B* of such a strength that *m* litres of it diluted to *a* litres give a solution containing *n* grams of sulphuric acid per litre. The number of grams *x* of water which must be added to any quantity *p* grams of sulphuric acid *A* of sp. gr. *S* and percentage strength 100*a*, in order to prepare the solution *B*, may be calculated approximately by means of equation (i), $mt.[pa/(p+x)] = an$ (i), in which *t* is the sp. gr. of a mixture of *p* grams of sulphuric acid with *x* grams of water. Assuming that the sp. gr. of a sulphuric acid-water mixture is a linear function of its composition, the equation (ii) will hold $(p+x)/t = p/S + x$ (ii); by combining this with equation (i) the third equation $mpaS = an(p+xS)$ (iii) is obtained. From the latter, the value of *x* may be calculated, and hence also the percentage of sulphuric acid may be deduced. Reference to the table gives the sp. gr. *t* corresponding with this strength of acid; on substituting this value of *t* in equation (i) *x* may be again determined. P. H.

Variable Sensitiveness in Colorimetry. III. DAVID W. HORN and SUE A. BLAKE (*Amer. Chem. J.*, 1906, 36, 516—521. Compare this vol., ii, 253, 703).—Ammoniacal solutions of copper sulphate exhibit the same phenomena as those observed in the cases studied previously. The results of the investigation are tabulated and plotted as curves.

The data so far obtained suggest the following generalisations. I. Equal weights of coloured solutes do not produce equal differences in colour except when they are added to coloured solutions of equal concentration. II. The weight of coloured solute required to produce a perceptible difference in colour when added to a coloured solution varies greatly with the concentration of the solution, and varies in an irregular manner, but the general behaviour is the same in all cases and is independent of the colour under examination. In the case of the most concentrated solutions which can be used in colorimetry, the sensitiveness varies inversely as the concentration. At a certain point of dilution this law ceases to be valid, and the weight of coloured solute required to produce a perceptible difference in colour rapidly becomes a smaller fraction of the total weight of coloured solute present, attains and passes through a minimum limiting value, and then rapidly becomes an increasingly larger fraction of the total solute present. All colorimetric analyses should be made within this second range. III. In the case of very faintly coloured solutions, the sensitiveness is much less and the percentage

error proportionately greater; such solutions should therefore be avoided in colorimetric analysis. E. G.

Analysis of Gases Rich in One or more Constituents.

ALFRED STOCK and CARL NIELSEN (*Ber.*, 1906, **39**, 3389—3393).—Attention is drawn to the errors which may arise in the analysis of gases owing to the air contained in the absorbing liquids. This is particularly noticeable in the case of pure oxygen, using either alkaline ferrotartrate or copper gauze in the presence of ammonia and ammonium carbonate. The latter reagent is better as it acts more quickly. When the freshly-prepared reagent is employed, a residue of 1.03 c.c. of nitrogen is obtained from 100 c.c. of pure oxygen. If a series of determinations are conducted one after the other, the amount of residue gradually decreases, until after the seventh estimation it is as low as 0.11 c.c. and remains at practically this value in subsequent estimations. This value corresponds with the state of equilibrium between the air on the one side of the solution, the solution and the oxygen on the other side. In order to prevent the reagent from rapidly dissolving nitrogen, the surface exposed to the air may be covered with a layer of liquid paraffin. Experiments have shown that when water free from air is poured from one vessel into another by means of a funnel, it rapidly absorbs gases, thus 1360 c.c. of water exposed for two minutes to the air in this way absorbed 5.8 c.c. of gas.

Analyses of pure oxygen made when the free side of the absorbing liquid was in contact with oxygen gave practically no residue, but when this oxygen was replaced by nitrogen a residue of 0.74 per cent. of nitrogen was obtained after twenty-one hours. J. J. S.

Volhard Method for the Estimation of Chlorine in Potable Waters. FRANK T. SHUTT and H. W. CHARLTON (*Trans. Roy. Soc. Canada*, 1905, [ii], **11**, (3), 67—71).—A comparison of the values of the chromate and Volhard's methods for the estimation of chlorine in potable waters. The latter is by far the more trustworthy.

G. Y.

Separation of Chlorine and Bromine in Acid Solution by Hydrogen Peroxide. PAUL JANNASCH (*Ber.*, 1906, **39**, 3655—3659. Compare this vol., ii, 194).—The solution of the mixture is placed in a glass flask fitted with a ground stopper, through which pass a delivery tube, a long inlet tube for passing in carbon dioxide, and a dropping funnel. The delivery tube is attached to a series of four flasks, each containing an ammoniacal solution of hydrazine sulphate. A mixture of concentrated sulphuric acid and water is run into the flask, and then 30 c.c. of a 6 to 8 per cent. hydrogen peroxide solution. Carbon dioxide is passed slowly through the flask, which is heated by means of a water-bath quickly brought to the boil. The heating by means of the gently boiling water-bath is continued until the liquid in the flask is colourless (0.5—0.75 hour). The contents of the receivers are mixed, acidified with nitric acid, and the hydro-

bromic acid precipitated as silver bromide. The results obtained are good, but usually slightly low.

The most important factor appears to be the concentration of the sulphuric acid, as if this is too low, only part of the bromine is driven over.
J. J. S.

Volumetric Estimation of Iodides in the presence of Chlorine and Bromine Ions. ERWIN RUPP and M. HORN (*Arch. Pharm.*, 1906, 244, 405—411).—When the estimation is effected by adding a ferric salt and distilling off the iodine, it is important that ferric sulphate (iron alum), not chloride, should be used.

Iodides, whether in the presence or in the absence of bromide or chloride, or of both, can be estimated without need for distillation. A weighed quantity of the sample (usually 0.2—0.5 gram) is dissolved in about 50 c.c. of water in a stoppered glass bottle; about 25 c.c. of dilute sulphuric acid are added, then about 3 grams of solid oxalic acid, and, finally, 1 per cent. potassium permanganate solution (usually about 10 c.c.). The mixture is allowed to remain for about three hours, being shaken occasionally in order to promote the solution of the manganese peroxide that has separated; then about 1 gram of potassium iodide is added, and the free iodine is titrated with *N*/10 thiosulphate. If an iodide is being titrated in the absence of bromide or chloride, the permanganate can be added until a distinct violet colour is visible in the thin layer of liquid seen at the top when the bottle is swung round. In the presence of bromides or chlorides, this guidance is not available; should decidedly less than 10 c.c. of the thiosulphate be used in the titration, the result must be rejected and the estimation repeated, either more of the substance or less of the permanganate solution being taken.

C. F. B.

The Etching Tests for Small Amounts of Fluorine. ALPHEUS G. WOODMAN and HENRY P. TALBOT (*J. Amer. Chem. Soc.*, 1906, 28, 1437—1443).—The solution is mixed with a little potassium sulphate and precipitated with barium acetate, and the precipitate, which contains also the barium fluoride, is tested as usual by the well-known etching test. The authors have found that in the case of very minute quantities the method may be rendered somewhat quantitative by observing the temperature required to produce the \perp -etch on the covering glass within an hour. A temperature of 79—82° distinguishes between 1:25000 and 1:100000; of 113° between 1:100000 and 1:1000000; of 136° between 1:1000000 and 1:5000000; of 173—178° between 1:5000000 and 1:25000000; of 213—218° between 1:25000000 or less.

For details of working, the original article and illustration should be consulted.
L. DE K.

Iodometric Estimation of Fluorine. ALBERT HILLMAN (*Amer. J. Sci.*, [iv], 22, 383—384).—The hydrofluosilicic acid obtained by distilling a fluoride with silica and sulphuric acid and collecting the silicon fluoride in water is mixed with potassium iodate-iodide

mixture and boiled in a flask having a glass stopper and connected with a trap containing solution of potassium iodide. When cold, the two solutions are united and the iodine liberated is titrated. One atom of iodine is liberated for every atom of fluorine present, as hydrofluosilicic or hydrofluoric acid. The results are approximately correct.

L. DE K.

[Fluorine in] Thermal Springs. JOSÉ CASARES (*Ber.*, 1906, 39, 3783—3784. Compare this vol., ii, 80).—A reply to Sahlbom and Hinrichsen (this vol., ii, 716, 798).

G. Y.

A Test for Oxygen. ANASTASIOS C. CHRISTOMANOS (*Chem. Centr.*, 1906, ii, 1139—1140; from *Verh. Ges. Deut. Naturf. Aerzte.*, 1905, ii, 76—77).—A sensitive reagent for oxygen is prepared by the action of phosphorus tribromide on solid copper nitrate, or on a solution not containing more than 10 per cent. of the salt; the mixture is then cooled and shaken with ether, when it gradually becomes colourless; it can be preserved in sealed vessels. On shaking with oxygen, the ether assumes a green colour and the lower layer becomes a reddish-purple; both colours, however, disappear after some minutes, and the reagent can then be used again. The reagent can also be employed for the detection of acetylene.

P. H.

Gravimetric Estimation of Ozone; Ozone Numbers of Oils. P. FENAROLI (*Gazzetta*, 1906, 36, ii, 292—298).—When ozonised air or oxygen is passed through oleic acid or linseed oil contained in a simple absorption apparatus comprising five bulbs, the absorption of the ozone is quantitative for wide limits of temperature (10 — 40°), and of velocity (up to 180 bubbles per minute); as the absorptive liquid loses slightly in weight, a calcium chloride tube should be attached beyond the bulbs. The increase in weight of the absorption bulbs corresponds exactly with the addition of the molecule O_3 for every double linking in, or more exactly, for every two atoms of iodine fixable by, the compound employed.

This absorption of ozone affords a convenient means of estimating it, the results obtained being virtually identical with those yielded by the potassium iodide method.

Determinations of the ozone numbers of olive, maize, linseed, and castor oils, the last two in solution in hexane from petroleum, give values agreeing well with those calculated from the iodine numbers.

T. H. P.

Estimation of Sulphur in Pyrites. MAX DENNSTEDT and F. HASSLER (*Zeit. angew. Chem.*, 1906, 19, 1668—1669).—Dennstedt's process, burning the sample in oxygen and absorbing the gaseous products in anhydrous sodium carbonate (*Abstr.*, 1905, ii, 761), is preferred to Lunge's nitrohydrochloric acid method (*Abstr.*, 1905, ii, 350).

L. DE K.

New Apparatus for the Estimation of Sulphur and Carbon. A. KLEINE (*Zeit. angew. Chem.*, 1906, 19, 1711—1712. Compare *Abstr.*, 1903, ii, 694; 1905, ii, 856).—*Estimation of Sulphur.*—The

apparatus consists of a conical flask sealed to an elongated separating funnel. When the substance has been introduced, the lower part of the funnel is closed by means of a perforated stopper furnished with an exit tube bent twice at right angles. The funnel is filled up to a definite mark with acid, which is then made to flow into the flask by turning the stopper and so creating a channel. The stopper is now put back into its original position, and the funnel is filled with water, which then serves as a cooling arrangement, the condensed acid flowing back into the flask.

Estimation of Carbon [in iron].—The main improvement is that the iron or steel borings are placed in a little bucket which is suspended inside the usual apparatus, consisting of a long-necked flask furnished with a bulb air-tube, and having a cooling arrangement placed inside the neck. At the right moment the bucket is turned over by an easy manipulation, and is taken out as soon as the experiment is finished. In this manner the same quantity of sulphuric-chromic acid mixture may suffice for even six estimations. L. DE K.

Sulphate and Sulphur Determinations. SALOMON F. ACREE (*J. Biol. Chem.*, 1906, 2, 135—143. Compare Folin, this vol., ii, 123).—Barium sulphate is readily reduced to the sulphide. If the filter paper is ignited with the sulphate, the amount of sulphide is considerable, and several evaporations with concentrated sulphuric acid are necessary in order to convert the whole of the sulphide into sulphate. The strength of a solution of sulphuric or hydrochloric acid can be determined by neutralising a given weight of pure sodium hydrogen carbonate with the acid, using methyl-orange as indicator, evaporating the solution in a platinum vessel and weighing the sodium salt. In titrating carbonates, the acid should be run in until the pink colour corresponds with the shade of a similar volume of water saturated with carbon dioxide and containing the same amount of indicator.

The strength of a solution containing pure sodium or potassium hydroxide or carbonate can be determined by adding an excess of hydrochloric acid to a known volume, evaporating down, and weighing the metallic chloride. Wildenstein's volumetric method gives good results.

Calcium or sulphates may be estimated by precipitation as calcium sulphate from aqueous-alcoholic solutions. J. J. S.

Iodometric Estimation of Hydrazine Salts and their Use in Volumetric Analysis. ENRICO RIMINI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 320—325. Compare Abstr., 1904, ii, 207).—The method previously given by the author for estimating hydrazine (*loc. cit.*) may be simplified by carrying out the reaction in an alkaline medium, the change then being represented by the equation $3\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4 + 2\text{KIO}_3 + 6\text{KOH} = 3\text{N}_2 + 2\text{KI} + 3\text{K}_2\text{SO}_4 + 12\text{H}_2\text{O}$. Gasometric estimation, by displacement of the air in a Lunge nitrometer, shows that the evolution of nitrogen is rapid and complete when iodic acid is employed.

In estimating formaldehyde by Riegler's method (Abstr., 1901,

ii, 360), it is advisable to titrate the excess of hydrazine with iodate in alkaline solution, since formalazine is not perfectly stable in an acid medium.

The estimation of mercuric salts by means of hydrazine is best carried out as follows. A concentrated solution of hydrazine sulphate, the strength of which need not be known, is rendered neutral to methyl-orange. A known excess of seminormal sodium hydroxide is added and then the solution of the mercuric salt of which the strength is required. The solution is next heated, and afterwards either made up to a certain volume and the alkalinity of an aliquot part determined, or filtered and the alkalinity of the filtrate and washings measured. When mercuric chloride is used, the reaction is expressed by $\text{N}_2\text{H}_4 \cdot \text{NaHSO}_4 + 2\text{HgCl}_2 + 5\text{NaOH} = 4\text{NaCl} + 2\text{Hg} + \text{N}_2 + 5\text{H}_2\text{O}$.

The best method for estimating persulphates is to add to a solution of the persulphate, neutral to methyl-orange, first a solution of hydrazine sulphate neutralised with potassium hydroxide, and then a known volume of potassium hydroxide solution of definite titre. The liquid is then shaken, and after five minutes the excess of alkali is determined. The reaction is represented by the equation $2\text{K}_2\text{S}_2\text{O}_8 + \text{N}_2\text{H}_4 \cdot \text{KHSO}_4 + 5\text{KOH} = \text{N}_2 + 5\text{K}_2\text{SO}_4 + 5\text{H}_2\text{O}$. This method is sensitive and rapid, and can be applied to ammonium salts, in the case of which Tarugi's method (Abstr., 1903, ii, 238) introduces complications.

T. H. P.

Detection of Nitric Acid. PAUL SOLTSIEN (*Chem. Centr.*, 1906, ii, 1020—1021; from *Pharm. Zeit.*, 51, 765—766).—Both the diphenylamine and the brucine reactions are interfered with by the presence of nitrous acid. When testing for nitric acid by reducing with zinc and then testing for nitrous acid, the reduction should not be pushed too far, as otherwise the formation of starch iodide may be prevented. In the presence of such substances as ferric or manganic oxides, the test with *m*-phenylenediamine should be applied. Attention is called to the presence of traces of nitrates in filter paper.

L. DE K.

Estimation of Nitrogen in Saltpetre. W. VAN DAM (*Rec. trav. chim.*, 1906, [ii], 25, 291—296).—Débourdeaux's method for the estimation of nitrogen in nitrates, which is based on the oxidising action of nitric acid on oxalic acid in the presence of manganese sulphate (Abstr., 1903, ii, 573), invariably gives results which are too high, owing to some of the oxalic acid undergoing oxidation by the atmospheric oxygen in the presence of the manganese sulphate; the author finds that the method is quite satisfactory if the air of the apparatus is replaced by carbon dioxide; and that the addition of one drop of a very dilute solution of potassium nitrite to the mixture containing the nitrate accelerates the reaction, which otherwise does not start for several hours when the nitrate under analysis is quite pure.

M. A. W.

Gravimetric Estimation of Potassium Nitrate in Meat. CARL PAAL and GUSTAV MEHRTENS (*Zeit. Nahr. Genussm.*, 1906, 12, 410—416).—Busch's method for the estimation of nitric acid by means

of "nitron" (Compare Abstr., 1905, ii, 282) may be applied to the estimation of potassium nitrate in meats. Fifty grams of the finely minced meat are treated with warm water for two hours, the mixture is then boiled, decanted, and the residue extracted with small quantities of water until the extracts no longer give a reaction with diphenylamine. The extracts are made up to a volume of 500 c.c., of which 200 c.c. are evaporated to a volume of about 50 c.c., treated, when cold, with three drops of ammonia and an excess of normal lead acetate. After boiling, the mixture is cooled and the precipitate collected on a filter and washed. The filtrate is acidified with acetic acid, heated, and the nitrate precipitated by the addition of "nitron" dissolved in acetic acid. One part of "nitron" nitrate is equivalent to 0.26933 part of potassium nitrate.

W. P. S.

Analysis of Sodium Nitrate (Chili Saltpetre). P. BECK (*Zeit. anal. Chem.*, 1906, 45, 669—686).—The quantity of sodium nitrate in Chili saltpetre is best estimated by Ulsch's method (Abstr., 1891, ii, 617). From the results of analyses given it is seen that the "indirect" method for determining the nitrate gives results which are too high; in some cases the figures are 1.5 per cent. higher than those obtained by Ulsch's method. It is pointed out that, as some samples of Chili saltpetre contain such quantities of perchlorate (compare Abstr., 1905, ii, 115) as render them unfit for the manufacture of sodium nitrite, the amount of sodium chloride in sodium nitrate intended for this purpose should not exceed 1 per cent., even after the sample has been fused with sodium carbonate or other substance capable of converting the perchlorate into chloride.

W. P. S.

Detection of Small Quantities of White Phosphorus in Presence of Large Quantities of Phosphorus Sesquisulphide. LOUIS ARONSTEIN (*Chem. Centr.*, 1906, ii, 977—978; from *Chem. Weekblad*, 3, 493—499. Compare this vol., ii, 705).—Van Eyk's lead acetate process (*ibid.*, 358) is untrustworthy. The method of rubbing in the dark the carbon disulphide extract is sensitive up to 1.4 per cent. of phosphorus. Vignon's method, treating in a current of hydrogen and observing the green flame, and also the brown coloration with silver solution, may be recommended.

L. DE K.

Titration of Phosphoric Acid. LUDWIG SCHUCHT (*Zeit. angew. Chem.*, 1906, 19, 1708—1711. Compare this vol., ii, 610).—Data are recorded which show that the estimation of free phosphoric acid in superphosphate solutions by titration with $N/2$ alkali and methyl-orange as indicator is considerably influenced by the dilution.

On addition of a large quantity of sodium chloride to a pure phosphoric acid solution, the acid titre is increased. This increase is more marked if calcium dihydrogen phosphate is present in the solution, and is still larger in the case of superphosphate solutions containing dissolved iron and aluminium.

By taking into account the various ions in solution and applying

the law of mass action, it is shown that the theoretical effect of the addition of sodium chloride is to increase the H^+ dissociation of the phosphoric acid as a consequence of the diminution in the concentration of H_2PO_4' ions. In superphosphate solutions the soluble phosphates present diminish the H^+ dissociation of the free acid, and in consequence the effect of the addition of sodium chloride is in this case more marked than in solutions of the pure acid. H. M. D.

Platinum Gauze for Contact Action in Organic Ultimate Analysis. W. C. HERAEUS (*Chem. Centr.*, 1906, ii, 907; from *Zeit. chem. Apparatenkunde*, 1, 541—542).—The apparatus consists of a spiral coil of platinum gauze which is covered with finely-divided platinum, and is encased for protection in a sheath of similar platinum gauze; it just fills the combustion tube and exerts a powerful contact action at comparatively low temperatures. P. H.

Determination of the Calorific Value of Lignite and Peat with the Lewis-Thomson Calorimeter. ROBERTO SALVADORI (*Gazzetta*, 1906, 36, ii, 202—211).—The calorific value of lignite, peat, coke, or anthracite cannot be accurately determined by the ordinary method of using the Lewis-Thomson calorimeter, since these fuels are not completely burnt by the mixture of potassium chlorate and nitrate employed. If, however, 1 part of ammonium nitrate is added to the usual mixture of 3 parts of chlorate and 1 of nitrate of potassium, these fuels undergo regular and ready combustion. When 2 kilos. of water are used, its temperature is raised 0.54° by each gram of ammonium nitrate employed. The latter salt should be fused, powdered, and kept for use in presence of calcium chloride.

Comparative determinations were carried out with (1) the Thomson calorimeter, using 1 gram of ammonium nitrate and 20 grams of the mixture of potassium chlorate and nitrate to 2 grams of the powdered fuel, and (2) the calorimetric bomb of Mahler. The results obtained by the two methods were found to agree to within 5 per cent.

The reaction between potassium chlorate and ammonium nitrate takes place at 123 — 124° according to the equation $KClO_3 + NH_4NO_3 = KNO_3 + NH_4ClO_3$, the ammonium chlorate formed then immediately decomposing into ammonium chloride, chlorine, a small proportion of oxygen, nitrogen, and oxides of nitrogen. To the activity of these products the ready combustion of the fuel is due. T. H. P.

Examination of Liquid Carbon Dioxide. WERDER (*Chem. Zeit.*, 1906, 30, 1021—1022).—Before taking a sample for analysis, the steel cylinder containing the liquid carbon dioxide should be inverted in order to mix the contents, as any air which may be contained in the cylinder would float on the carbon dioxide. A sufficiently large sample should be analysed so that the residual gas remaining after absorption with potassium hydroxide measures at least 4 c.c.; this may require from 2 to 4 litres. The gas should be measured out in successive portions of 200 c.c., each one

being passed into the potassium hydroxide burette and absorbed before introducing the next. The following are suggested to be the requirements of liquid carbon dioxide: it should not have a pungent odour, and should have a purely acid taste; it should contain at least 98 per cent. of carbon dioxide, but not more than 0.5 per cent. of carbon monoxide; it should not contain any sulphurous or nitrous acids, and should not decolorise acid permanganate when bubbled through this solution for a quarter of an hour, nor should it produce a precipitate when bubbled through a solution of silver nitrate acidified with nitric acid.

P. H.

Estimation of Carbon Dioxide. H. REBENSTORFF (*Chem. Zeit.*, 1906, **30**, 1114—1115).—The apparatus described by the author (this vol., ii, 487), when filled with sodium nitrate solution of sp. gr. 1.35, can be employed for estimating carbon dioxide. The carbon dioxide in the generating apparatus is displaced by means of hydrogen, produced by adding a known weight of magnesium to the acid; the volume of carbon dioxide is obtained by deducting the volume of hydrogen so evolved from the total volume of gas collected.

P. H.

Analysis of Hydrofluosilicic Acid. LUDWIG SCHUCHT and W. MÖLLER (*Ber.*, 1906, **39**, 3693—3696. Compare Sahlbom and Hinrichsen, this vol., ii, 798).—According to Offermann, hydrofluosilicic acid may be titrated with cochineal as indicator according to the equation $\text{H}_2\text{SiF}_6 + 6\text{KOH} = 6\text{KF} + \text{H}_4\text{SiO}_4 + 2\text{H}_2\text{O}$, and, according to Weise, with phenolphthalein as indicator, according to the equation $\text{H}_2\text{SiF}_6 + 2\text{KOH} = \text{K}_2\text{SiF}_6 + 2\text{H}_2\text{O}$. The reverse is, however, the case, since the action with cochineal is represented by the latter equation and that with phenolphthalein by the former. When cochineal is used, the end point is not sharp. When phenolphthalein is used, the titration must be conducted with hot solutions.

If an excess of neutral calcium chloride is added to the solution of hydrofluosilicic acid, the end point is sharp when the titration is conducted with sodium hydroxide with methyl-orange as indicator. The action is represented by the equation $\text{H}_2\text{SiF}_6 + 3\text{CaCl}_2 + 6\text{NaOH} = 3\text{CaF}_2 + 6\text{NaCl} + \text{H}_4\text{SiO}_4 + 2\text{H}_2\text{O}$.

A. McK.

New Qualitative Test for Calcium. FRED F. FLANDERS (*J. Amer. Chem. Soc.*, 1906, **28**, 1509—1511).—The acetic acid solution of carbonates of barium, strontium, and calcium obtained in due course, is freed from barium by addition of potassium chromate and the filtrate is again precipitated with ammonia and ammonium carbonate. The precipitate is collected, washed, and dissolved in a little acetic acid and the liquid divided into two portions. One portion is tested for strontium with solution of calcium sulphate and the other for calcium by adding an equal volume of ammonium chloride solution and then a few c.c. of potassium ferrocyanide which gives a light, yellowish-green precipitate of potassium calcium ferrocyanide.

L. DE K.

A New Calcimeter. NAPOLEONE PASSERINI (*Chem. Centr.*, 1906, ii, 1019; from *Staz. sperim. agrar. ital.*, 39, 28—32).—The apparatus consists of a funnel, *a*, furnished with a stopcock, *b*, which is placed on a tube, *d*, of larger diameter which carries on two knobs, *e e'*, a movable tube, *c*, at the bottom of which is placed the carbonate or the soil to be tested. The tube, *d*, is closed with the rubber cork, *f*, and connected by means of the stopcock *g* with the graduated tube, *h*.

L. DE K.



Quantitative Separation of Glucinum from Aluminium. BORIS GLASSMANN (*Ber.*, 1906, 39, 3366—3367).—The solution containing the glucinum and aluminium salts is neutralised with sodium carbonate, an excess of sodium thiosulphate added and the solution boiled until the odour of sulphurous acid has disappeared. The precipitated aluminium hydroxide and sulphur are washed and ignited whilst in the filtrate, the excess of thiosulphate is decomposed by hydrochloric acid, and the glucinum precipitated by ammonia or the iodine-iodate mixture (see following abstract).

E. F. A.

Estimation of Glucinum. BORIS GLASSMANN (*Ber.*, 1906, 39, 3368—3369).—To a neutral or faintly acid solution of the glucinum salt a mixture of equal parts of 25 per cent. potassium iodide and saturated potassium iodate solution is added; after five minutes the iodine which has separated is decolorised by 20 per cent. sodium thiosulphate and a small quantity more of the iodine-iodate mixture added. The solution is then heated on the water-bath for half an hour and the colourless flocculent precipitate of glucinum hydroxide filtered, washed with hot water, dried, and ignited.

E. F. A.

Volumetric Estimation of Mercury. ERWIN RUPP (*Ber.*, 1906, 39, 3702—3704. Compare Rupp and Krauss, *Abstr.*, 1902, ii, 475).—A modification of the author's earlier method (*Abstr.*, 1905, ii, 484). The mercury solution (25—50 c.c., which should contain about 0.2 gram of the metal) is mixed with potassium iodide until the precipitate first formed is redissolved; it is then made alkaline with an alkali hydroxide, and shaken vigorously while 2—3 c.c. of pure formaldehyde and 10 c.c. of water are added; after 30—60 seconds it is strongly acidified with acetic acid and the estimation carried out as described previously (*loc. cit.*). Mercurous salts must first be converted into mercuric salts, by the addition either of bromine or of permanganate.

A. McK.

Insolubility of Ferric Hydroxide in Ammoniacal Solutions. GREGORY P. BAXTER and ROBERT A. HUBBARD (*J. Amer. Chem. Soc.*, 1906, 28, 1508—1509).—The authors had previously noticed a case in which the ferric hydroxide precipitate redissolved to a considerable extent in the excess of commercial ammonia added; it was, however,

recovered by expelling the excess of ammonia. The cause of this solution taking place has not been determined, but experiments show that it cannot have been occasioned by the presence of amines in the ammonia used.

L. DE K.

New Delicate Test for Nickel. Nickeldicyanodiamidine. HERMANN GROSSMANN and BERNHARD SCHÜCK (*Ber.*, 1906, 39, 3356—3359).—The solution of a nickel salt added to dicyanodiamide, which has been heated previously with a few drops of acid, followed by potassium hydroxide, yields a dense yellow, crystalline precipitate of *nickel dicyanodiamidine*, $\text{Ni}(\text{C}_2\text{H}_5\text{ON})_2 \cdot 2\text{H}_2\text{O}$, composed of stellar aggregates of characteristic needles. The salt becomes flesh-coloured when heated and is very sparingly soluble in water and ammonia. Concentrated solutions of nickel salts yield this precipitate at once, dilute solutions when boiled or kept; cobalt salts do not give any such precipitate.

E. F. A.

Estimation of Uranium and Vanadium. A. N. FINN (*J. Amer. Chem. Soc.*, 1906, 28, 1443—1446).—The sample of ore representing about 0.25 gram of uranyl oxide is heated with sulphuric acid until sulphuric acid fumes are given off. The mass is dissolved in water and precipitated while boiling with excess of sodium carbonate. The precipitate is freed from uranium by redissolving in sulphuric acid and reprecipitating with sodium carbonate. The combined filtrates are heated to boiling, and after adding 0.5 gram of ammonium phosphate a slight excess of ammonia is added. After boiling for a few minutes longer, the precipitate is collected and washed with a weak solution of ammonium sulphate.

The filtrate which contains the vanadium is acidified with sulphuric acid, reduced with sulphur dioxide, and after boiling off the excess of the latter, titrated with permanganate. The precipitate containing the uranium is also titrated with permanganate after being first reduced by means of zinc and dilute sulphuric acid.

L. DE K.

[Volumetric Estimation of] Antimony in Babbit and Type Metals. H. YOCKEY (*J. Amer. Chem. Soc.*, 1906, 28, 1435—1437).—One gram of the finely divided alloy, supposed to contain no more than 7 per cent. of copper, is boiled with 40 c.c. of water, 40 c.c. of fuming hydrochloric acid, and 1 gram of potassium iodide for one hour, and the undissolved antimony is collected on an asbestos filter and well washed with hot, dilute hydrochloric acid (1 : 10).

The asbestos and its contents are now heated in a beaker with 25 c.c. of hydrochloric acid and a little potassium chlorate until the antimony is dissolved. Water is added up to 100 c.c., the solution is filtered and the asbestos well washed. The free chlorine is expelled by boiling the solution vigorously for five minutes, and when cold 1 gram of potassium iodide is added, and the liberated iodine titrated with thiosulphate as usual.

L. DE K.

Electrolytic Precipitation of Gold with the Use of a Rotating Anode. JAMES R. WITHROW (*J. Amer. Chem. Soc.*, 1906, 28, 1350—1357).—Experiments have been made with the object of study-

ing the rate of electrolytic precipitation of gold from solutions of the chloride in presence of potassium cyanide or sodium sulphide, a rotating anode being employed. The results, which are tabulated and plotted as curves, show that potassium cyanide is a better electrolyte for this purpose than sodium sulphide, although the latter gives very satisfactory results.

Attention has also been given to the electrolytic estimation of alkali haloids (compare Smith, Abstr., 1903, ii, 755). In order to obtain the iodine as an adherent deposit, the spiral cathode was rotated at 300—500 revolutions per minute, and a silver-plated dish was employed as the anode. Excellent results were obtained with potassium iodide and also with potassium chloride. E. G.

Detection of Sophistication in Wine. GEORGES HALPHEN (*Bull. Soc. chim.*, 1906, [iii], 35, 879—906).—The applicability of Gautier's "sum of alcohol and acid" rule in its modified form (Abstr., 1901, ii, 353) is discussed in the light of the results of the examination of 5400 samples of wines of different origin, and curves showing the minimum values of the ratio, acid/alcohol, for various types of wines are given.

The last section of the paper gives details of the methods suggested (Gautier and Halphen, Abstr., 1903, ii, 564) for distinguishing between alcoholic liquors prepared artificially and those which have been obtained by fermentation. T. A. H.

Separation of Animal from Vegetable Cholesterol. ADOLF WINDAUS (*Chem. Zeit.*, 1906, 30, 1011. Compare this vol., i, 580).—When a mixture of cholesterol and phytosterol dissolved in ether is treated with a solution of bromine in glacial acetic acid, a crystalline precipitate of dibromocholesterol is formed, from which the cholesterol may be recovered by reduction with zinc dust and acetic acid; the filtrate from the dibromocholesterol contains dibromophytosterol, which may be reduced similarly to give phytosterol. P. H.

Unification of the Methods of Estimating Lactose in Milk. GUSTAVE PATEIN (*Bull. Soc. chim.*, 1906, [iii], 35, 1022—1030).—A *résumé* is given of the methods proposed by Poggiale, Méhu, Esbach, Villiers, Adams, and Patein (Abstr., 1902, ii, 291, 536) and that used in the Municipal Laboratory of Paris, and from a consideration of these it is concluded that: (1) the process of estimation by means of Fehling's solution is alone applicable to all milks; (2) the purified lactose solution used for the titration should occupy ten times the volume of the sample of milk taken; (3) the results should be expressed as anhydrous lactose; (4) in applying the polarimetric method of estimation to cow's milk, the latter should be defecated with the nitro-mercuric reagent; (5) one saccharimetric degree may be taken as equal to 1.96 grams of anhydrous lactose. T. A. H.

Estimation of Sugars by Means of the Refractometer. LUCIUS M. TOLMAN and M. B. SMITH (*J. Amer. Chem. Soc.*, 1906, 28, 1476—1482).—Instead of determining the sugar contents of a solution by means of the specific gravity, the authors prefer to determine the

index of refraction with an Abbé refractometer. (The butyrefractometer cannot be employed for this work.) Reference is then made to tables constructed by the authors.

L. DE K.

Influence of Lead Salts on the Polarimetric Investigation of Urine and Organic Secretions. HERMANN GROSSMANN (*Chem. Centr.*, 1906, 11, 1141—1142; from *Biochem. Zeit.*, 1, 339—353).—Alkaline lead solutions greatly affect the rotatory power of dextrose, lævulose, galactose, lactose, and maltose, but β -hydroxybutyric acid is but little, and lactic acid, conjugated glycuronic acids, and glucosides are scarcely, affected. In practice, therefore, all alkaline liquids should be slightly acidified with acetic acid and precipitated with normal lead acetate.

L. DE K.

Microscopic Examination of Starch and Detection of Rice Starch in Wheat Starch. EUGÈNE COLLIN (*J. Pharm. Chim.*, 1906, [vi], 24, 385—395).—Microscopically, wheat-starch is composed of small round or oval granules and large lenticular granules either isolated or aggregated in groups of granules of unequal size. The aluerone grains, which do not stain blue, are aggregated in granules of equal size. The irregular masses of gluten are also characteristic. Rice starch consists of simple granules sometimes showing a hilum, of complicated oval granules and of meal-like masses of cells. It contains relatively few aluerone granules, and the gluten behaves differently to that of wheat. To detect rice-starch in wheat, 33.33 grams of flour are made into a ball with 17 grams of water and worked between the fingers in a fine stream of water over a fine-meshed sieve. The starch and waste water are well shaken and set aside for twelve hours in a large conical flask, when the starch separates in three well-marked layers which can be separated by decantation. The top layer contains most of the small starch granules, and the bottom layer the largest grains, whereas the middle layer is mainly composed of the cellulose and proteid element of the flour; when rice starch is present it is almost entirely deposited in this layer, and its presence can be detected in so small a proportion as 1 per cent.

E. F. A.

Estimation of Cellulose, Lignin, and Cutin in Crude Fibre. JOSEF KÖNIG (*Zeit. Nahr. Genussm.*, 1906, 12, 385—395).—The following method is proposed for the separation and estimation of the constituents of the crude fibre obtained by the method described previously by the author (*Abstr.*, 1903, ii, 764). A second portion of the sample is treated with hydrogen peroxide and ammonia under the conditions given (*ibid.*). The residue remaining after this treatment is collected on an asbestos filter and washed. Both residue and filter are now subjected to the action of ammoniacal cupric oxide solution for two hours. The mixture is then gently warmed and the residue collected on an asbestos filter, washed, dried at 110°, and weighed. The filter and its contents are next ignited and again weighed. The loss in weight gives the amount of cutin present. The ammoniacal filtrate from the cutin residue is mixed with 300 c.c. of 80 per cent. alcohol

and well stirred; the dissolved cellulose is reprecipitated and is collected on an asbestos filter, dried at 110° , weighed, ignited, and the filter reweighed. The difference between the total crude fibre and the sum of the cutin and the cellulose gives the quantity of lignin.

W. P. S.

Mangin's Ruthenium-Red as a Reagent for Pectins. F. TOBLER (*Chem. Centr.*, 1906, ii, 1020; from *Zeit. wiss. Mikrosk.*, 23, 182—186).—Mangin's reagent, an ammoniacal solution of ruthenium sesquichloride, also gives a coloration with glycogen and isolichenin, and is, therefore, not a trustworthy test for pectins. L. DE K.

Detection of Formaldehyde in Milk. SALOMON F. ACREE (*J. Biol. Chem.*, 1906, 2, 145—148).—The purple coloration produced in Hehner's, or Richmond and Boseley's modification of Hehner's, test for formaldehyde in milk is due to the presence of casein and lactalbumin; the same coloration is produced by most complex proteids, and is most pronounced with the globulin from squash seeds. The addition of a small amount of this globulin to milk renders it possible to detect formaldehyde by the Richmond and Boseley test even with concentrations less than 1 in 250,000.

The depth of colour increases with the amount of casein present.

J. J. S.

Presence of Formaldehyde in certain Food-Stuffs. GUSTAVE PERRIER (*Compt. rend.*, 1906, 143, 600—602).—By means of the sensitive colour reaction for formaldehyde, described by Voisenet (this vol., ii, 59), the author has found that the amount of this compound present in cider and various smoked foods varies from 0.04 mg. to 2.6 mg. per 100 grams. In view of this fact, and the facts that formaldehyde is present in air (Henriet, Abstr., 1904, i, 648; ii, 598) and in products of combustion (Trillat, Abstr., 1905, ii, 53, 325; this vol., i, 234), it is urged that the present (French) laws and regulations inhibiting absolutely the use of formaldehyde as a food preservative should be revised. M. A. W.

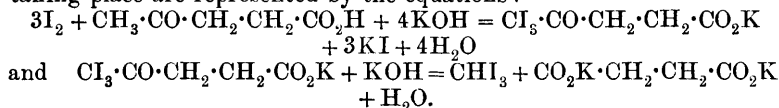
Estimation of Citral in Lemon Oils and Extracts. EDWARD MACKEY CHACE (*J. Amer. Chem. Soc.*, 1906, 28, 1472—1476).—Twenty to thirty grams of lemon extract or 2 grams of lemon oil are diluted to 100 c.c. with 95 per cent. aldehyde-free alcohol (this vol., i, 393) at 15° . Four c.c. of the solution are then placed in comparison tubes side by side with tubes containing 4 c.c. of standard citral solution; 20 c.c. of alcohol are added, then 20 c.c. of reduced magenta solution and then alcohol up to 50 c.c. After being placed in a water-bath at 15° for ten minutes the colours are compared, best by direct matching. The results are highly satisfactory for the extracts, but less so for the oils.

The standard citral solution is prepared by diluting 1 gram of pure citral to 1 litre with 50 (vol.) per cent. alcohol. The magenta solution is prepared by dissolving 0.5 gram of the dye in 100 c.c. of water and adding 16 grams of dissolved sulphur dioxide; when decolorised, water is added up to 1 litre.

L. DE K.

Titration with Permanganate in Alkaline Solution. [**Estimation of Formic and Nitrous Acids.**] ERWIN RUPP (*Zeit. anal. Chem.*, 1906, 45, 687—692).—The oxidation of formic acid by permanganate takes place much more rapidly in alkaline than in acid solution; whilst in the former the reaction is complete in thirty minutes, in the latter it is incomplete after the lapse of ten hours. For the estimation, a measured volume of the formic acid (or formate) solution, containing not more than 1 per cent. of the acid, is heated in a closed flask in a water-bath with the addition of an excess of *N*/10 permanganate solution and 0.5 gram of anhydrous sodium carbonate. After thirty minutes heating, the solution is acidified with sulphuric acid, potassium iodide is added, and the liberated iodine titrated with *N*/10 thiosulphate solution. Each c.c. of the latter corresponds with 0.0023 gram of formic acid. The oxidation of nitrous acid proceeds equally rapidly in alkaline and acid solutions, but the former is to be preferred as there is no danger of loss of nitrous acid. The reaction is complete in ten minutes at the ordinary temperature, and the estimation is carried out as in the case of formic acid. One c.c. of *N*/10 thiosulphate solution is equivalent to 0.0023 gram of NO_2 . W. P. S.

Iodometric Estimation of Lævulic Acid. B. SAVARÉ (*Gazzetta*, 1906, 36, ii, 344—348).—Being unable to prepare lævulic acid pure and free from the corresponding γ -lactone, the author uses crystalline calcium lævulate, $\text{Ca}(\text{C}_5\text{H}_7\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$, as a means of obtaining a known weight of lævulic acid. To a solution of calcium lævulate is added first a measured quantity of *N*/10 iodine in potassium iodide, and then a known volume, in excess, of normal potassium hydroxide free from nitrites. The liquid is shaken for a few minutes and, after the iodoform has settled, is filtered through a weighed Gooch crucible, on which the iodoform is washed until all alkali is removed. The reactions taking place are represented by the equations:



To the filtrate from the iodoform, *N*-hydrochloric acid is added in amount equivalent to the potassium hydroxide first added. The excess of iodine, which was combined with the potassium hydroxide, is thus set free and can be estimated by titrating with *N*/10 sodium thiosulphate. The iodine which has reacted with the lime to form CaI_2 and CaI_2O_6 remains, however, unchanged. One c.c. of *N*/10 iodine corresponds with 0.0019344 gram of lævulic acid.

The method gives accurate results, and may be employed for estimating the lævulic acid formed by the action of dilute acids on hexoses or that obtained by the oxidation of natural methylheptenone (Tiemann and Semmler, *Abstr.*, 1895, i, 646), geraniol, or linalool.

T. H. P.

Crystalline appearance of Calcium Tartrate as a Distinctive and Delicate Test for the Presence of Tartaric Acid or Tartrates. A. L. SULLIVAN and CHARLES A. CRAMPTON (*Amer. Chem. J.*, 1906, 36, 419—426).—The following method is described by means of

which the precipitate of calcium tartrate formed by the addition of calcium chloride to solutions of soluble tartrates can be obtained in rhombic prisms or pyramids which can be readily identified with the aid of the microscope. The paper is illustrated with plates showing the form of these crystals.

The solution to be tested should be concentrated but should not contain more than 30 per cent. of solid matter. About 50 c.c. of the concentrated solution are cooled, rendered slightly alkaline with potassium hydroxide, and treated with a few drops of 20 per cent. solution of potassium acetate and about 10 c.c. of 30—40 per cent. solution of calcium chloride. The mixture is stirred rapidly for a minute or two and left at the ordinary temperature for twelve to fifteen hours when, if tartaric acid is present, characteristic crystals of calcium tartrate are produced.

A study has been made of the effect on this test of the presence of citric, malic, succinic, oxalic, and aconitic acids, and it is found that in most cases the method is trustworthy. The presence of alum or excess of mineral acids, however, prevents the formation of the precipitate.

The test is recommended especially for the detection of tartaric acid in wines, ciders, and fruit syrups.

E. G.

Determination of the Saponification Number in Oils and Fats. J. DAVIDSOHN and G. WEBER (*Chem. Centr.*, 1906, ii, 1141; from *Seifensiederszeit.*, 33, 770—771).—One or two grams of the sample are dissolved in a little ether, 10 c.c. of 2*N*-potassium hydroxide and 25 c.c. of absolute alcohol are added, and the whole is boiled for fifteen minutes in a reflux apparatus. The solution is then titrated back with *N*-hydrochloric acid, using phenolphthalein as indicator.

L DE K.

A Method of Estimating Urea. H. D. HASKINS (*J. Biol. Chem.*, 1906, 2, 243—249).—A modification of the Mörner-Folin method.

W. D. H.

New Reaction of Aconitine. N. MONTI (*Gazzetta*, 1906, 36, ii, 477—480).—The greyish-violet coloration obtained by evaporating aconitine on the water-bath with sulphuric or phosphoric acid is due to the presence of impurities in the alkaloid, and up to the present no reaction has been given for aconitine which is not obtained with other alkaloids.

The following reaction detects 0.0001 gram of aconitine, for which it is specific if applied to sufficiently pure products of an alkaloidal nature. A small portion of the alkaloid (0.0002—0.001 gram) is placed in a porcelain capsule and treated with 2 to 4 drops of sulphuric acid of sp. gr. 1.75—1.76. If only aconitine is present, either no change or a faint yellow coloration is produced on heating the capsule for five to six minutes on a water-bath; but if a quantity of crystallised resorcinol about equal to that of the alkaloid taken is added and the heating continued, the liquid assumes a reddish-yellow colour, which gradually changes to an intense reddish-violet; this colour is very stable, and persists for a long time if the capsule is kept in a desiccator.

T. H. P.

[Volumetric] Assay of Cinchona Barks. ADALBERT PANCHAUD (*Chem. Centr.*, 1906, ii, 1212; from *Schweiz. Woch. Pharm.*, 44, 580—582).—The author observed that a chloroform solution of cinchona alkaloids rapidly becomes neutralised owing probably to the following reaction taking place: $\text{CHCl}_3 + \text{O} = \text{COCl}_2 + \text{HCl}$.

If it is intended to determine the alkaloids by titration, the chloroform should therefore at once be evaporated off. L. DE K.

Alkaloid Reactions [Codeine]. C. REICHARD (*Chem. Centr.*, 1906, ii, 1220—1221; from *Pharm. Centr.-Halle*, 47, 727—733).—A colourless crystal of codeine gives no colour with strong sulphuric acid. In contact with 30 per cent. nitric acid, the latter turns yellow. Twenty-five per cent. hydrochloric acid is not affected. With bismuth chloride, a dark yellow colour is produced; on adding aqueous potassium hydroxide, a reddish-brown precipitate is formed. A mixture of codeine and sodium arsenate turns gradually dark grey at the edges when heated with hydrochloric acid; on further addition of sulphuric acid, a yellow or greenish-yellow colour is generated. A mixture of codeine and ammonium molybdate with a drop of hydrochloric acid turns first yellow, afterwards blue. A mixture of codeine and α -naphthol gives no reaction with aqueous potassium hydroxide or hydrochloric acid, but on adding sulphuric acid a blue coloration is noticed, which increases on warming. A mixture of codeine and sodium iodate turns yellow on adding 25 per cent. hydrochloric acid. When a mixture of codeine and ammonium metavanadate is moistened with water and then dried, it turns bright yellow round the edges. If a mixture of crystals of codeine and mercurous nitrate is moistened with water, the codeine crystals turn dark grey and then turn reddish-brown on adding a drop of sulphuric acid. Several other reactions of less importance are given. L. DE K.

Estimation of the Alkaloids in the Leaves and Stalks of *Datura Arborea*. HEINRICH BECKURTS (*Chem. Centr.*, 1906, ii, 916; from *Apoth. Zeit.*, 21, 662).—Ten grams of the dried and powdered leaves or stalks are shaken with 90 grams of ether and 30 grams of chloroform, 10 c.c. of a 10 per cent. solution of sodium hydroxide are added, and the whole set aside for three hours with frequent shaking. Sufficient water is then added to make the powder form a coherent mass, and after the lapse of an hour, 60 grams (=5 grams of sample) are poured off and filtered through a dry filter. Of the filtrate, one-half is distilled to expel any ammonia, and the remaining liquid is shaken in a separating funnel with 10 c.c. of *N*/100 hydrochloric acid and then titrated back with *N*/100 potassium hydroxide, using iodo eosin as an indicator. The leaves contain on an average 0.444 and the stalks 0.226 per cent. of scopolamine.

L. DE K.

Alkaloid Reactions (Thebaine). C. REICHARD (*Chem. Centr.*, 1906, ii, 915—916; from *Pharm. Centr.-Halle*, 1906, 47, 623—629).—A small quantity of thebaine when treated with one drop of concentrated sulphuric acid turns brownish-yellow and then pure yellow. When

moistened with 25 to 30 per cent. nitric acid, thebaine slowly turns yellow, and as the colour darkens streaks are developed through the liquid. Concentrated hydrochloric acid likewise produces a yellow coloration with green streaks. A mixture of thebaine with copper sulphate is turned permanently green by 25 per cent. hydrochloric acid, whilst a mixture with mercuric chloride turns yellow and then grey. Thebaine may be distinguished from narcotine, narceine, or papaverine by the black coloration which is developed after half an hour on moistening a mixture of the alkaloid with mercurous nitrate.

Thebaine, when evaporated to dryness with stannous chloride and moistened with 40 per cent. potassium hydroxide, turns black or greenish-black; when treated in the same way with antimony chloride and potassium hydroxide, it turns yellow. When treated with a concentrated hydrochloric acid solution of bismuth chloride, it gives a yellow coloration, which is changed to reddish-brown by the addition of potassium hydroxide. A few drops of concentrated cobalt nitrate solution when warmed with thebaine gives a brown residue. A mixture of thebaine with diphenylamine, treated with one drop of concentrated sulphuric acid, turns dark reddish-brown and after some time green, whereas codeine under the same conditions remains colourless. A mixture of thebaine with α -nitroso- β -naphthol turns light green on addition of one drop of 25 per cent. hydrochloric acid; on evaporating to dryness the colour changes to violet. P. H.

Separation of Indole from Scatole and their Estimation. CHRISTIAN A. HERTER and M. LOUISE FOSTER (*J. Biol. Chem.*, 1906, 2, 267—271).—From a solution containing both substances, the indole can be completely removed as a naphthaquinone compound, and the scatole can then be distilled and recognised by Ehrlich's dimethylamino-benzaldehyde reaction. The estimations are colorimetric. W. D. H.

Analysis of Indigo. EDMUND KNECHT (*J. Soc. Dyers Colourists*, 1906, 22, 330—332; a reply to Bloxam. Compare this vol., ii, 818, 819, 820).—The author records the results of experiments which show that his method of titrating indigo with titanous chloride (*Abstr.*, 1905, ii, 872) is quite trustworthy. The concentration of the indigo solution and the strength of the titanous chloride solution within reasonable limits have no influence on the results obtained. W. P. S.

Detection of Indican in Urine by means of Alkali Persulphates. LUCIANO ROSSI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 309—311).—A solution of an alkali persulphate is a very sensitive reagent for indican in urine, but it must be used in small amount, otherwise no coloration may be obtained when indican is present. The best method of carrying out the test is to add to 5 or 6 c.c. of the urine an equal volume of concentrated hydrochloric acid and one drop of 10 per cent. potassium (or sodium or ammonium) persulphate solution. The formation of a violet-blue coloration, which, when ammonium persulphate is used, appears immediately, indicates the presence of indican. If 1 or 2 c.c. of chloroform are added to the tube, and the latter closed with the thumb and gently inverted two or

three times, the chloroform assumes a more or less intensely blue coloration according to the amount of indican present.

This method may also be applied to the estimation of indican by Wang's process. T. H. P.

Behaviour of Nessler's Reagent towards some Glucosides [Saponin] and Carbohydrates. LEOPOLD ROSENTHALER (*Chem. Centr.*, 1906, ii, 7174; from *Pharm. Centr.-Halle*, 47, 581).—In the cold, Nessler's reagent gives no reddish-yellow precipitate with the saponin from sarsaparilla, and but slowly a dirty, green precipitate with that from guaiacum. The precipitates formed on heating are the same for all saponins except that of sarsaparilla, which is but slowly acted on even on boiling. Salicin gives with Nessler's reagent in the cold a yellow, crystalline precipitate which scarcely changes its colour on warming. Amygdalin gives off ammonia, which then colours the reagent, whilst with other glucosides the carbohydrate group gives a reaction. Dextrose, levulose, xylose, maltose, also lactose (slowly) reduce the solution, and the yellowish-red precipitate soon becomes dark red, and finally green and greyish. Sucrose also gives reduction on boiling. L. DE K.

Qualitative Analysis of Tannins. MAXIMILIAN NIERENSTEIN (*Chem. Zeit.*, 1906, 30, 868).—The solution is mixed in the cold, drop by drop, with a one-half per cent. solution of diazobenzene chloride. Tannins belonging to the catechol group at once give a precipitate, whilst those belonging to the pyrogallol group do not (compare this vol., i, 446). L. DE K.

Estimation of Tannin. BOUDET (*Bull. Soc. chim.*, 1906, [iii], 35, 760—762).—This is a modification of the iodometric method devised by Jean (*Abstr.*, 1900, ii, 632). Four grams of iodine and 8 grams of potassium iodide are dissolved in water and the solution made up to 1 litre. The solution of sodium thiosulphate employed, contains 7.81 grams of the salt per litre. Each gram of iodine used is equivalent to 1.137 grams of tannin.

In carrying out the estimation 4.54 grams (4×1.137) of the tanning material are exhausted with boiling water, and the extract, after filtration, is made up to 1 litre. To 10 c.c. of this solution a like quantity of the iodine solution is added, and the mixture set aside for two hours. At the end of that time the excess of iodine is estimated by means of the sodium thiosulphate solution, using starch mucilage as an indicator. The quantity of iodine used, expressed in tenths of a c.c., is equal to the percentage of tannin in the tanning material.

The method is applicable to the estimation of tannin in catch, the end of the reaction being marked in this case by the liquid under titration becoming transparent.

Gallic acid may also be estimated by this process; 1 gram of iodine being equivalent to 0.467 gram of gallic acid, so that in preparing solutions for estimation, 0.467×4 grams of the crude material should be taken.

In estimating tannin and gallic acid in products containing both,

10 c.c. of a solution, prepared as for the estimation of tannin, is titrated in the usual way and the number of tenths of a c.c. of iodine solution used ($T+G$) noted. To a second 10 c.c., 1 gram of hide powder is added, the mixture is set aside for twelve hours, filtered, and the filtrate treated with iodine solution, titrated, and the number of tenths of a c.c. of iodine solution used (G_1) noted. The percentage of tannin present is equal to $T+G-G_1$, and that of gallic acid is given by $G_1 \times 0.041$.

T. A. H.

Rapid Estimation of Albumin in Urine. GEORG BÜCHNER (*Chem. Centr.*, 1906, ii, 717; from *Münch. med. Woch.*, 53, 1019—1020).—The urine is boiled in a specially graduated tube, a little brine is added, and a few drops of nitric acid. After one hour the volume of the coagulated albumin is read off.

L. DE K.

Means for Distinguishing True Albumin in Urine from Mucinoid Substances. LEON GRIMBERT and ÉMILE DUFAU (*J. Pharm. Chim.*, 1906, [vi], 24, 193—199).—The usual Heller (nitric) ring test is applied and also a second test, substituting syrupy citric acid for nitric acid. (1) If the urine contains mucinoids only, a more or less decided ring is formed with citric acid at the place of contact within one or two minutes, and often the whole of the supernatant urine becomes turbid; with nitric acid, however, no ring is visible at the place of contact, but a nebulous ring is formed a little above this. (2) If the urine contains pathological albumin only, no ring whatever is obtained with citric acid, but with nitric acid a ring is formed at the place of contact. (3) If the urine contains both mucinoids and albumin, reactions are obtained with both citric and nitric acids. These preliminary tests render it impossible to mistake mucinoids for albumin.

L. DE K.

Estimation of Proteid-Nitrogen contained in Beet-Molasses. ALBERT STUTZER and J. E. VON WOLOSEWICZ (*Zeit. anal. Chem.*, 1906, 45, 614—620).—Good approximate results may be obtained by dissolving 50 grams of the molasses in 300 c.c. of water and diluting the filtrate to 500 c.c., 100 c.c. are faintly acidified with alum solution and then mixed with 25 c.c. of Stutzer's cupric hydroxide emulsion and 100 c.c. of water. After five hours the deposit is collected and the nitrogen determined by the Kjeldahl process. There is as yet no satisfactory process for the separate determination of peptones and albumins in molasses.

L. DE K.

Estimation of Proteid in Human Milk. ALFRED W. SIKES (*J. Physiol.*, 1906, 34, 481—489).—Hot alcohol precipitates the proteids of human milk completely, and extracts the non-proteid constituents entirely. The addition of a small quantity of citric acid prevents any precipitation of salts. The precipitate is best washed by the use of the centrifuge; drying occurs rapidly, and the proteid is weighed directly. The percentage of proteid varies from 1.66 to 2.68.

W. D. H.